

Transformation of CO₂ to C₂₊ alcohols by tailoring the oxygen bonding via Fe-based tandem catalyst

Corresponding Author: Professor Mingbo Wu

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This study reports the successful synthesis of high yields of C₂₊ alcohols through CO₂ hydrogenation using a combination of FeCo alloy and a copper/zinc/aluminum (CZA) catalyst. The FeCo-CZA catalyst system achieved a 51.1% CO₂ conversion and a 49.1% selectivity towards C₂₊ alcohols at a reaction temperature of 320°C and a pressure of 5 MPa. The catalyst demonstrated excellent stability, maintaining performance for over 1000 hours of continuous operation. Additionally, the reaction mechanism was investigated using density functional theory (DFT) calculation and other analytical methods. Economic evaluations of the process were also conducted.

In order to improve the quality of the paper further, the manuscript needs revision addressing the following issues:

1. The catalyst demonstrating the best activity was the Fe-Co alloy. However, the introduction of the paper lacks sufficient literature discussion regarding the rationale for combining Co with Fe. In addition to the fact that Co was used based on the results of using various other metals, additional evidence is needed. Furthermore, the introduction should include citations from relevant literature to clarify the characteristics of Co compared to other metals that contribute to the observed results. In the analysis section, the discussion focusing on Co is insufficient, making it unclear what specific advantages Co provides to the reaction. This aspect requires more detailed analysis and explanation.
2. There is no explanation for the purposes of H₂-TPR, CO-TPD, and N₂ adsorption-desorption isotherm. For the analysis added to the paper, it is essential to explain in detail which information the authors like to acquire through the analysis.
3. When CZA was used with FeCo alloy, C₂₊ alcohols selectivity increased significantly, but the analysis of the role of CZA seems insufficient. It seems necessary to add analysis and explanation to highlight the role of CZA.
4. To clearly present the reaction mechanism, both in-situ DRIFT and DFT calculations must provide a cohesive perspective. While the DFT calculations appear to be performed in detail, the in-situ DRIFT analysis seems insufficient to support the proposed reaction mechanism. Notably, in-situ DRIFT was conducted using the spent catalyst rather than a fresh one. This choice is not well-justified, as no peak shifts were observed, and only an increase in peak intensity over time was reported. To support the DFT results and the proposed mechanism, in-situ DRIFT analysis using a fresh catalyst should be included in the paper.

Reviewer #2

(Remarks to the Author)

Wu et al. developed an excellent FeCo&CZA tandem catalyst for CO₂ hydrogenation to C₂₊ alcohols. Multiple characterization and comprehensive theoretical calculation have thoroughly verified that the controllable oxygen bonding behaviors on the interface of FeCo alloy carbide guarantees the outstanding catalytic performance (high C₂₊ alcohols selectivity of 49.1% at a CO₂ conversion of 51.1%) and long-term stability (>1000 h). The novel and detailed reaction mechanism proposed in this work is promising to shed new light on the rational design of highly efficient C₂₊ alcohols synthesis catalyst. Furthermore, the technical and economic analyses have confirmed the viability of this catalytic system in eliminating carbon emissions at practical application scale. Therefore, I recommend to publish this manuscript after addressing the following issues.

1. The influence of reaction conditions (such as temperature and pressure) on the catalytic performance should be investigated in detail.
2. Some new developments reported by other research groups should be updated and included in Figure 1c.

3. In supplementary Table 1, other transition metals (Zn/Mn/Cu) were also compounded with Fe-based active site. I wonder that if any alloy carbides were also formed.

4. It is obvious that the Fe/Co ratio is essential for alloy carbide formation, please explain this phenomenon in the main text.

5. High quality and comprehensive theoretical calculation is provided in this work, I suggest that the calculation details of Fe₅C₂(510) model should be provided in the main text to support the key point of oxygen bonding regulation.

6. Generally, the FeC_x component can directly dissociate CO to produce CH_x via a carbide mechanism. Has the authors considered this pathway in Fig. 4d?

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This study reports the successful synthesis of high yields of C₂+ alcohols through CO₂ hydrogenation using a combination of FeCo alloy and a copper/zinc/aluminum (CZA) catalyst. The FeCo&CZA catalyst system achieved a 51.1% CO₂ conversion and a 49.1% selectivity towards C₂+ alcohols at a reaction temperature of 320°C and a pressure of 5 MPa. The catalyst demonstrated excellent stability, maintaining performance for over 1000 hours of continuous operation. Additionally, the reaction mechanism was investigated using density functional theory (DFT) and other analytical methods. Economic evaluations of the process were also conducted.

The authors addressed well the issues I raised in my initial review report, but I can see there are still a few issues that have to be further addressed before the final acceptance:

1. The role of Co needs to be more clearly explained. The authors state that the incorporation of other metals along with Fe promotes the formation of the carbide phase, as evidenced by in-situ XRD and XPS analyses. However, the underlying mechanism by which Co specifically facilitates the formation of the carbide phase has not been sufficiently analyzed or discussed. A more detailed explanation, supported by appropriate references, is necessary to clarify the effect of Co.

2. The comparison between FeCo and Fe catalysts in the in-situ DRIFTS results needs to be more convincing. Although the authors discuss the role of Co based on differences observed in the fingerprint region (Fig. S26), it is difficult to clearly distinguish such differences from the data presented. The distinctions between the two catalysts must be shown more explicitly in order for the authors' claims regarding Co's effect to be convincing.

3. While the authors make various claims based on their experimental results, these claims should be supported by relevant references to enhance their clarity and credibility. The addition of supporting literature would help solidify the arguments presented.

Reviewer #2

(Remarks to the Author)

the revised manuscript is satisfactory to me and can be published.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have addressed well my additional concerns, and I am satisfied with their response and relevant revision. Now I recommend acceptance of the revised manuscript for publication in nat. commun. in the current form.

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Reviewer #1 (Remarks to the Author):

This study reports the successful synthesis of high yields of C₂₊ alcohols through CO₂ hydrogenation using a combination of FeCo alloy and a copper/zinc/aluminum (CZA) catalyst. The FeCo-CZA catalyst system achieved a 51.1% CO₂ conversion and a 49.1% selectivity towards C₂₊ alcohols at a reaction temperature of 320 °C and a pressure of 5 MPa. The catalyst demonstrated excellent stability, maintaining performance for over 1000 hours of continuous operation. Additionally, the reaction mechanism was investigated using density functional theory (DFT) calculation and other analytical methods. Economic evaluations of the process were also conducted. In order to improve the quality of the paper further, the manuscript needs revision addressing the following issues.

Response: Many thanks for the reviewer's comments. We are grateful to receive the reviewer's comments and suggestions, which are very helpful for us to improve our manuscript. According to the reviewer's suggestion, we have revised our manuscript carefully, and the detailed changes were deduced as follows.

1. The catalyst demonstrating the best activity was the Fe-Co alloy. However, the introduction of the paper lacks sufficient literature discussion regarding the rationale for combining Co with Fe. In addition to the fact that Co was used based on the results of using various other metals, additional evidence is needed. Furthermore, the introduction should include citations from relevant literature to clarify the characteristics of Co compared to other metals that contribute to the observed results. In the analysis section, the discussion focusing on Co is insufficient, making it unclear what specific advantages Co provides to the reaction. This aspect requires more detailed analysis and explanation.

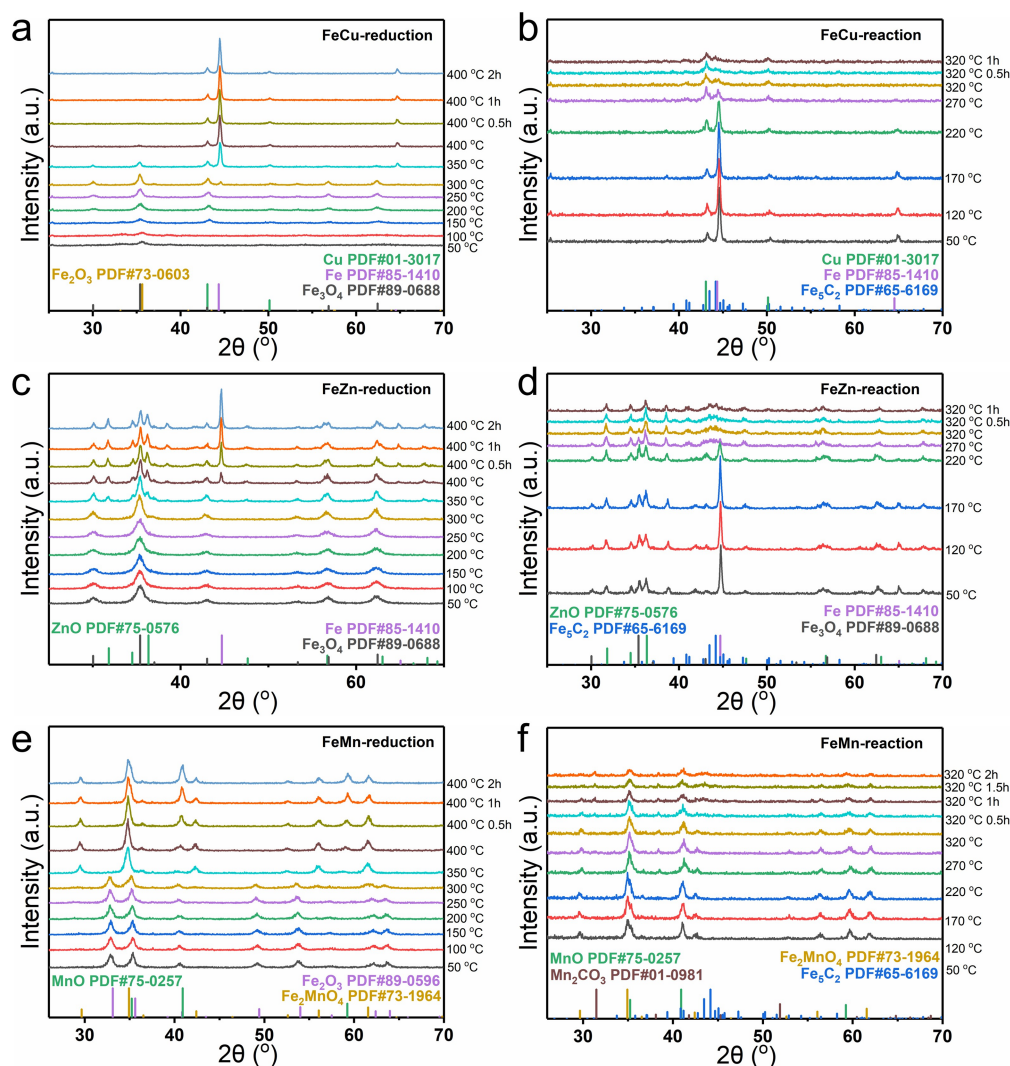
Response: Thanks for the reviewer's comment. Your comments are very constructive and has pointed out the shortcomings in the introduction and analysis sections of the manuscript. Below are specific improvements targeting these issues:

(1) Increase the literature discussion to clarify the rationale for selecting Co as follow:

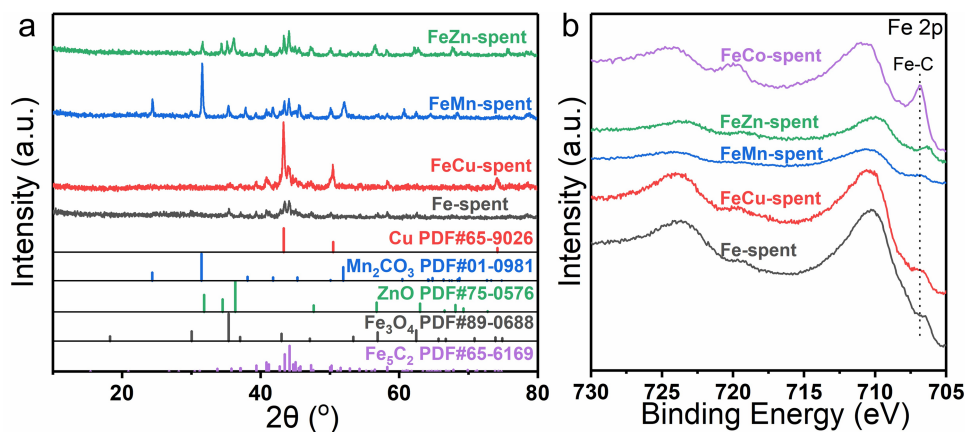
“The alloy carbide is the optional measure to regulate the electronic structure of Fe. The cobalt (Co) is well-known for its excellent catalytic activity in CO/CO₂ hydrogenation reactions^{19,21,22,25,26}. Unlike Fe being converted to Fe₃O₄ to some extent during CO₂ hydrogenation, Co or cobalt carbide (Co₂C) remains predominantly, indicating lower O affinity of Co compared to Fe^{16,19,21,22,27}. In addition, both the elements of Co and Fe belong to the family of transition metals, with adjacent atomic numbers and similar chemical properties. Co (3d⁷4s²) has one more 3d electron than Fe (3d⁶4s²) allows for electronic structure modulation, that is a unique advantage that facilitates the formation of FeCo alloy carbides, further contributing to its catalytic efficiency for CO₂ hydrogenation to C₂+OH.

(2) Supply more evidences by in-situ XRD and XPS for series bimetal FeX catalysts in the analysis section as follow:

“Other bimetal FeX catalysts are not satisfactory. The phase evolution of bimetal FeX catalysts during reduction and reaction processes was monitored by in-situ XRD (Supplementary Fig. 1). The phases of Cu, MnCO₃, ZnO were detected on spent bimetal FeX catalysts, indicating the alloy carbide formed difficultly by these metals (Supplementary Figs. 1 and 2a). As illustrated in Fe2p XPS spectra, the binding energy of Fe-C bond in FeCo alloy carbide was higher than that of other FeX catalysts, suggesting the bonding ability of Fe and C was stronger than those of other FeX catalysts (Supplementary Fig. 2). The formation of FeCo alloy carbides led to lattice stress effect, which affected the electronic structure of Fe atoms.”



Supplementary Fig. 1. The in-situ XRD patterns of (a) FeCu reduction, (b) FeCu reaction, (c) FeZn reduction, (d) FeZn reaction, (e) FeMn reduction, and (f) FeMn reaction. Reduction conditions: H_2 flow rate of 60 ml min^{-1} . Reaction conditions: 0.8 MPa, $\text{H}_2/\text{CO} = 2$, 80 ml min^{-1} .



Supplementary Fig. 2. (a) XRD patterns and (b) XPS spectra of series spent catalysts.

2. There is no explanation for the purposes of H₂-TPR, CO-TPD, and N₂ adsorption-desorption isotherm. For the analysis added to the paper, it is essential to explain in detail which information the authors like to acquire through the analysis.

Response: We thank for the reviewer's suggestions. We have supplemented the explanation of H₂-TPR, CO-TPD, and N₂ adsorption-desorption isotherm on **page 7** in the revised manuscript, as follows:

“In addition, the H₂-temperature programmed reduction (TPR), CO-temperature programmed desorption (TPD) (Supplementary Fig. 11) and N₂ adsorption-desorption isotherm (Supplementary Fig. 12, Supplementary Table 7) also verified the structure changes. In H₂-TPR, the Fe catalyst evolved from the initial α -Fe₂O₃ through Fe₃O₄, FeO, and finally to metallic Fe. The FeCo catalyst exhibited the reduction peak for the initial FeCo alloy oxide phase to FeCo alloy. The position of the reduction peaks obviously shifted toward the lower temperature, suggesting that the addition of Co element could improve the reduction ability of the FeCo catalysts. The carburization behaviors of catalyst were monitored by CO-TPD, the position of the peaks obviously shifted toward the higher temperature, indicating that the carburization of FeCo metallic phase was difficult than that of Fe catalyst, corresponding to the results of XRD (Supplementary Fig. 10b). The surface area of FeCo catalyst was larger than that of Fe catalyst, and the mesopore structure was dominant. After the reaction, the surface area of FeCo-spent and Fe-spent was similar.”

3. When CZA was used with FeCo alloy, C₂₊ alcohols selectivity increased significantly, but the analysis of the role of CZA seems insufficient. It seems necessary to add analysis and explanation to highlight the role of CZA.

Response: Thanks for the reviewer's kind reminder. To further highlight the role of the CZA catalyst, we have provided a more detailed discussion on the CO₂ hydrogenation mechanism over CZA (see Page 13-14) and have moved Supplementary Fig. 22 into the main text (Fig. 4a). It is demonstrated that CZA can effectively and selectively generate CH_xO* species, including the key intermediate CH₂O*, which is crucial for the following C-C coupling process. This occurs with a lower energy barrier of 1.03

eV, compared to 1.39 eV on the FeCo alloy carbide. In-situ DRIFTS of CZA catalyst was performed (Fig. 4b), the signal of CO was dominant, corresponding well to the catalytic performance of the reverse water-gas shift (RWGS) reaction. The HCOO*, CHO* and CH₂O* signals were also detected, that reconfirmed the supplement of abundant CH_xO* species.

Notably, we found that the diffusion or spillover of CH₂O* from the CZA surface can occur readily, with a small energy barrier ranging from 0.20 to 0.24 eV (Supplementary Fig. 23). Therefore, when CZA is integrated with Fe-based catalysts or FeCo alloy carbide, it can supply an abundance of CH_xO* intermediates to the active Fe-based carbides. This promotes the coupling between CH_x* and CH_xO* species, thereby enhancing the formation of C₂+OH products. CZA alone is not active for producing C₂+OH, as indicated by the relatively high energy barriers for the coupling of CH₂* with CH₂O* (0.53 eV), and especially between two CH₂O* species (1.22 eV), as shown in Supplementary Fig. 24.

We also designed a series of Fe/CZA and FeCo/CZA catalysts with varying CZA loadings and evaluated their catalytic performances (Supplementary Fig. 4 and Supplementary Table 4). The catalytic activity of the FeCo&CZA system significantly improved as the FeCo-to-CZA ratio decreased from 16:1 to 2:1. In contrast, the performance of the Fe&CZA system remained relatively insensitive to the CZA composition ratio. These results clearly indicated that FeCo carbide could provide unique active sites that efficiently facilitated the coupling of CH_xO* and CH_x* species, thereby enhancing alcohol formation more effectively than the Fe-based counterpart.

In addition, we found that the presence of CZA could significantly promote the carburization of the FeCo alloy as confirmed by XRD analysis (Supplementary Fig. 10), likely due to the generation of carbon-containing species such as CO* via RWGS reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) on CZA component, which can be employed as carburization species.

The supplemented manuscript was as follows:

Page 14:

“However, once the CZA (K₂O/Cu(111)/ZnO(101)) component was introduced, the

catalytic performance was significantly enhanced, underscoring the critical role of CZA in promoting alcohol production. To further unveil the role of CZA in C_2+OH synthesis from CO_2 hydrogenation, the reaction mechanism of CO_2 hydrogenation into C_1 products on the interface of CZA was finally studied (Fig. 4a, Supplementary Table 15). Our computations indicated that the adsorption of CO_2 on the interface was energetically favorable with a downhill energy of -0.80 eV. Once the CO_2^* was formed, CO_2^* was readily protonated by H^* to form $HCOO^*$ with an energy barrier of 0.63 eV. Subsequently, the CZA preferred to catalyze the CO_2 hydrogenation via the following steps: $CHOO^* \rightarrow CH_2OO^* \rightarrow CH_2O^* + O^* \rightarrow CH_2O^* + OH^* \rightarrow CH_2O^* + H_2O^* \rightarrow CH_2O^* + H_2O(l) \rightarrow CH_3O^* \rightarrow CH_3OH^* \rightarrow CH_3OH$. The rate limiting step was identified as the $CH_2O^* + O^* \rightarrow CH_2O^* + OH^*$ with a smaller energy barrier (1.03 eV) than that of $(Fe_{3/4}Co_{1/4})_5C_2(510)$. In addition, by comparison with CH_2O^* hydrogenation (0.27 eV) and CH_2O^* spillover (ca. 0.20 to 0.24 eV), the CZA itself was less inclined to generate C_2+OH via the coupling of CH_2^* and CH_2O^* (0.53 eV), or the self-coupling between two CH_2O^* species (1.22 eV), as shown in Supplementary Figs. 23 and 24. Therefore, the critical role of CZA in the designed tandem catalysts should be an important reaction intermediates supplier to provide abundant CH_xO^* species via fast spillover process. What's more, the formed CO from RWGS process at CZA surface could also be directly used as the reactant to participate in the C_2+OH synthesis, and contribute to the improvement of the catalytic performance (Figs. 3a and 3b). In-situ DRIFTS of CZA catalyst was performed (Fig. 4b), the signal of CO was dominant, corresponding to the catalytic performance via the RWGS reaction. The $HCOO^*$, CHO^* and CH_2O^* signals were also detected, that reconfirmed the supplement of abundant CH_xO^* species.”

“However, when the Co content was increased to 50% (Fe/Co = 1:1), both the alloy carbide and FeCo alloy phases were observed in the FeCo(1:1)-spent catalyst. This indicates that an excessive amount of Co is unfavorable for the carburization process. In contrast, the FeCo(1:1)&CZA-spent catalyst exhibited complete carburization of the metallic phase. This suggests that the presence of CZA could significantly promotes the carburization of the FeCo alloy, likely due to the generation of carbon-containing species such as CO* via the reverse water-gas shift (RWGS) reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) on CZA component, which can be employed as carburization species.”

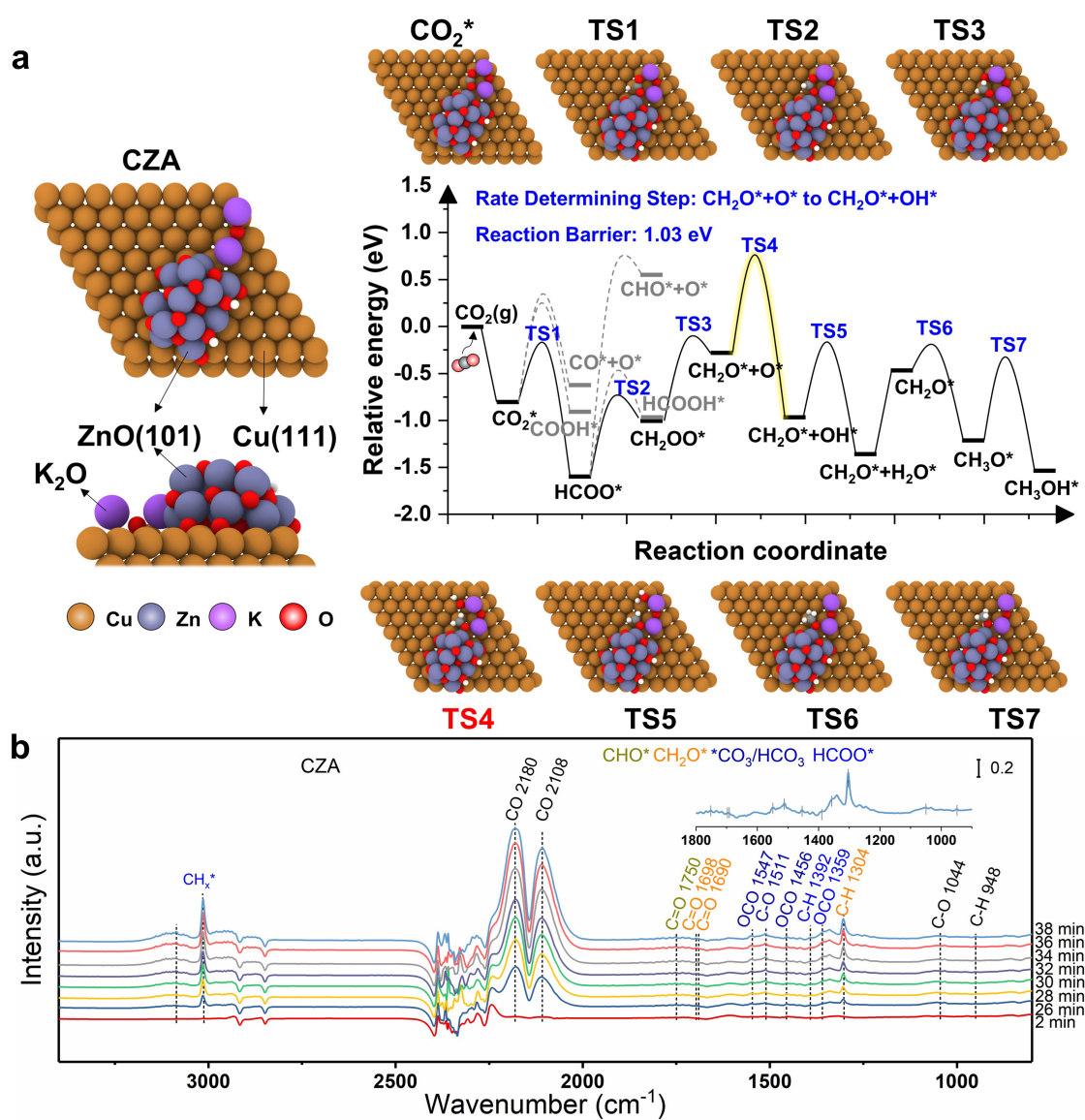
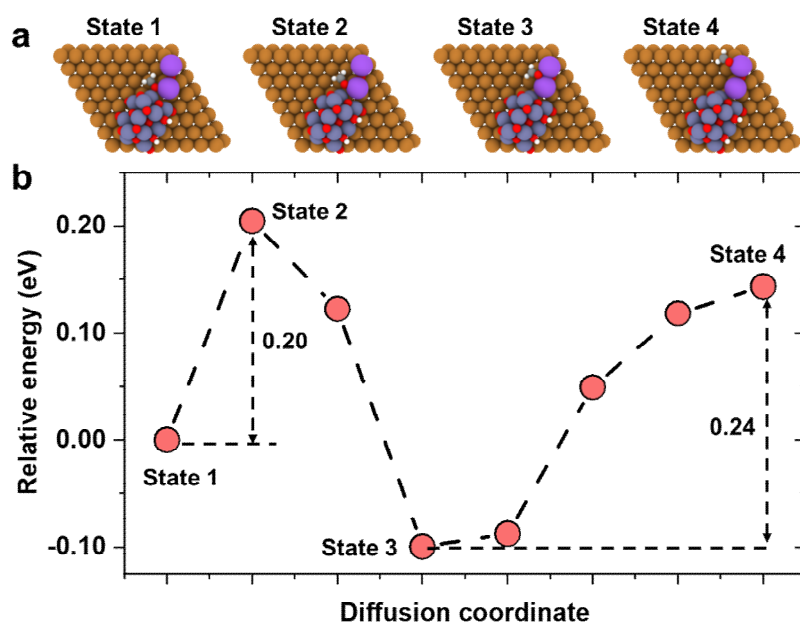
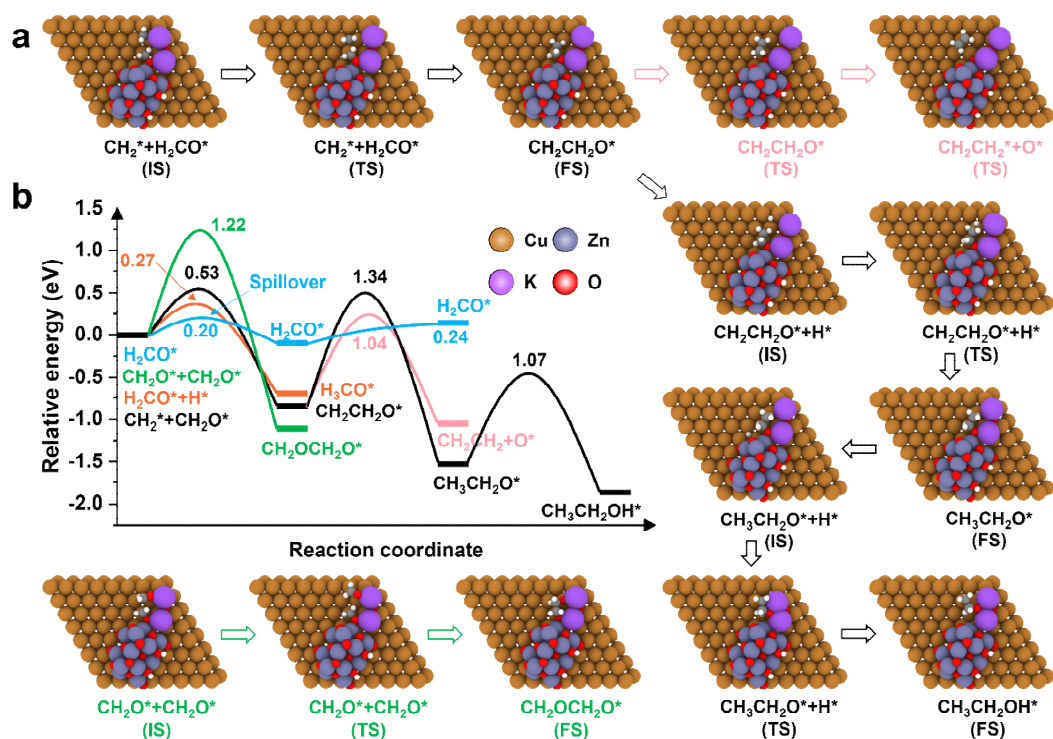


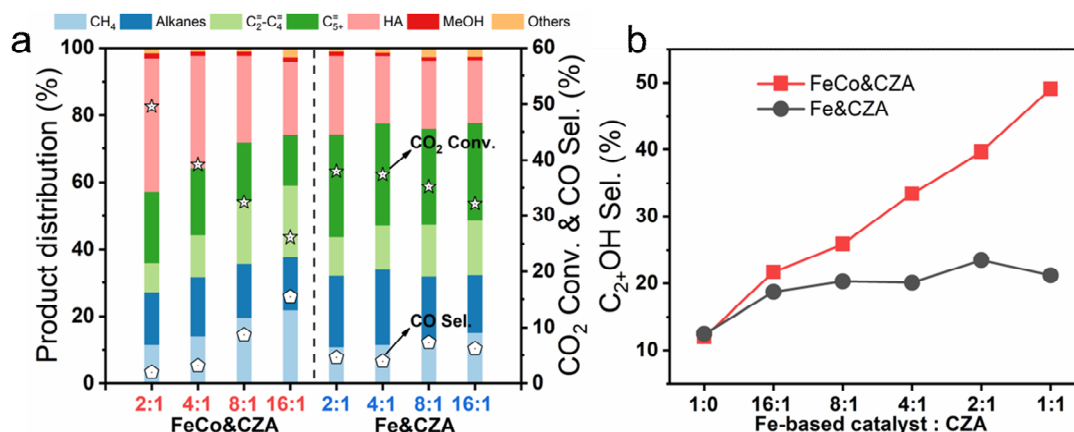
Fig. 4 | (a) Reaction paths of CO₂ hydrogenation on the interface of K₂O/Cu(111)/ZnO(101) and (b) In-situ DRIFTS of CZA catalyst.



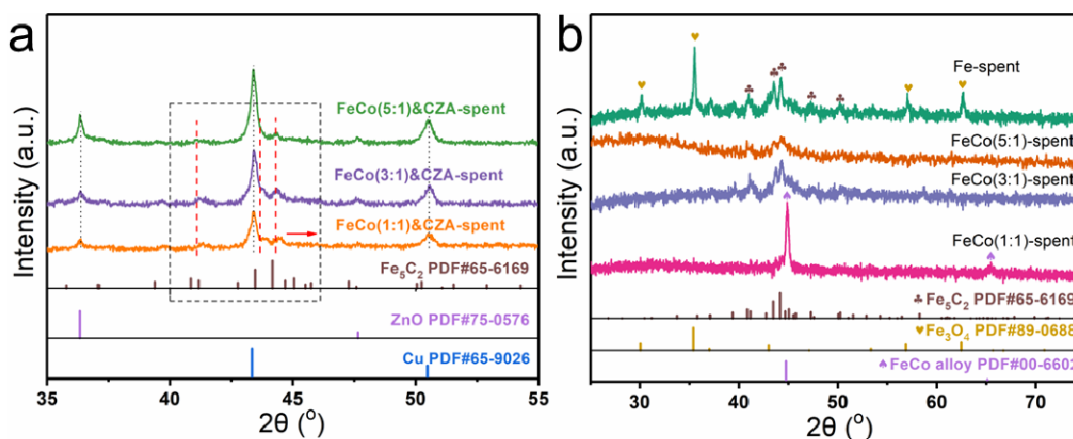
Supplementary Fig. 23. The diffusion/spillover pathways of CH_2O^* on the interface of $\text{K}_2\text{O}/\text{Cu}(111)/\text{ZnO}(101)$.



Supplementary Fig. 24. Reaction pathways of C-C coupling and the corresponding kinetic barrier of each elementary step on the interface of K₂O/Cu(111)/ZnO(101). For comparison, the energy barrier of spillover for CH₂O* species is also shown.



Supplementary Fig. 4. The reaction performance of the multifunctional catalysts with different CZA weights. Reaction conditions: 320 °C, 5.0 MPa, H₂/CO₂ = 3:1, Fe-based catalyst of 0.1g and the weight of CZA is 1/x of Fe-based catalyst, TOS = 8h, 4500 ml g_{cat}⁻¹ h⁻¹.



Supplementary Fig. 10. XRD patterns of (a) FeCo&CZA-spent catalysts with different ratios of Fe/Co, and (b) Fe-spent catalyst and FeCo-spent catalysts with different ratios of Fe/Co.

4. To clearly present the reaction mechanism, both in-situ DRIFT and DFT calculations must provide a cohesive perspective. While the DFT calculations appear to be performed in detail, the in-situ DRIFT analysis seems insufficient to support the proposed reaction mechanism. Notably, in-situ DRIFT was conducted using the

spent catalyst rather than a fresh one. This choice is not well-justified, as no peak shifts were observed, and only an increase in peak intensity over time was reported. To support the DFT results and the proposed mechanism, in-situ DRIFT analysis using a fresh catalyst should be included in the paper.

Response: We thank the reviewer for noticing this issue. The in-situ DRIFTS analysis using fresh catalysts have been supplemented. The reaction mechanism was analyzed further. We have supplemented the explanation for in-situ DRIFTS analysis on **page 16** in the revised manuscript, as follows:

“In-situ DRIFTS was performed to monitor the important intermediates during the CO₂ hydrogenation reaction under reaction conditions of 320 °C and 5 MPa. For the FeCo&CZA catalyst (Fig. 5a), carbonate (CO₃) and bicarbonate (HCO₃*) with typical bands at 1455, 1510, and 1547 cm⁻¹ were observed. The bands appeared at 1357 and 1392 cm⁻¹ evidenced the formation of formate species (HCOO*). The bands at 1303, 1689, and 1697 cm⁻¹ can be attributed to the stretching vibration of C=O and the deformation vibration of C-H in CH₂O*. CHO* was also detected at 1750 cm⁻¹. The stretching vibrations of C=C (1649 cm⁻¹) and C-H (3050~3150 cm⁻¹) can be corresponded to the unsaturated alkenes. The RWGS reaction was confirmed with the appearance of gas phase CO (2108 and 2180 cm⁻¹). The stretching vibration of C-O in alcohols was observed at 1044 cm⁻¹, and the bands between 2897 and 2966 cm⁻¹ can be attributed to the stretching vibration of C-H in C₂H₅O*⁴²⁻⁴⁷. In comparison, there was almost no presence of C=C band and C₂H₅O* on CZA only, implying that pure CZA catalyst did not catalyze multi-carbon products synthesis (Fig. 4b and Supplementary Fig. 26). The peak intensity of gas phase CO (2108 and 2180 cm⁻¹) delivered from CZA catalyst dominated, which stemmed from RWGS reaction. The peak intensity of gas phase CO delivered from the Fe&CZA catalyst strengthened, whereas the typical bonds for C-O in alcohols weakened, which can be attributed to the cleavage of C-O bond in O-containing intermediates due to strong O-bonding ability. It comprehensively verifies that the absence of Co in the catalyst is detrimental for C₂+OH synthesis due to the reduced coverage of O-containing intermediates on the catalytic*

interface (Supplementary Fig. 26).

The C-O bonds on the fingerprint region ($1200\sim 1900\text{ cm}^{-1}$) that derived from the FeCo catalyst were more abundant than that from the Fe catalyst (Supplementary Fig. 26), indicating that the introduction of Co could promote the formation of O-containing intermediates, which can be attributed to the effect of Site 1 (Fig. 3a) on the surface of FeCo alloy carbide. Theoretical computations indicated that the addition of Co can effectively tailor the O-bonding ability of iron carbide, which is important to control the cleavage of C-O bond in O-containing intermediates and produce C_{2+} alcohols (Fig. 3). In contrast, once CH_xO^* adsorbed on the surface of Fe_5C_2 , the cleavage of the C-O bonds in CH_xO^* was preferential, leading to the formation of hydrocarbons by coupling of CH_x^* species (Figs. 3c and 3d). Therefore, the absence of Co in the catalyst is detrimental for C_{2+}OH synthesis due to the reduced coverage of O-containing intermediates on the catalytic interface. This is the reason why the intensity of CH_xO^* for FeCo&CZA is stronger than that of Fe&CZA as confirmed by in-situ DRIFTS.”

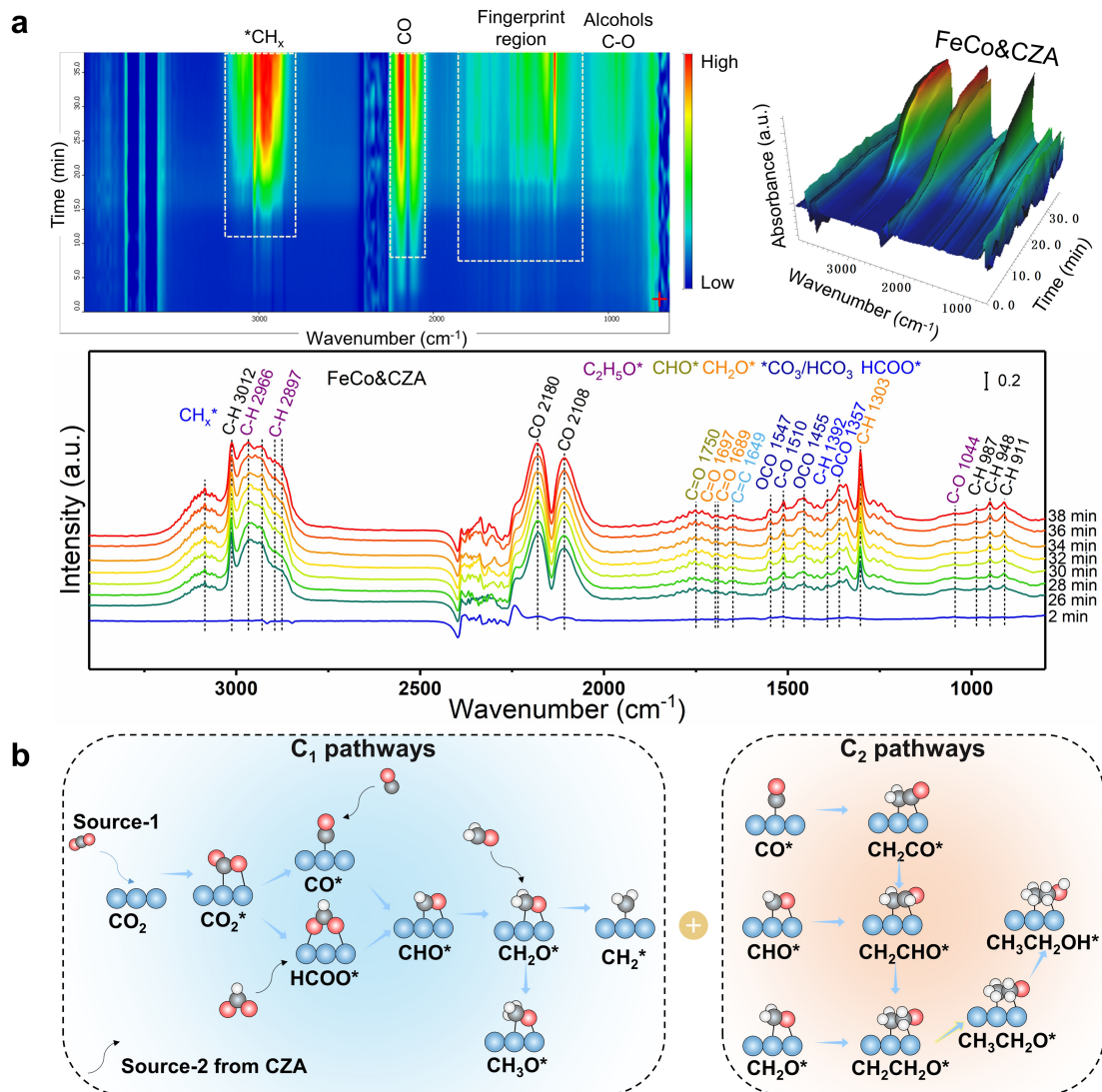


Fig. 5 | Reaction mechanism for C₂+OH synthesis on the FeCo&CZA catalyst. (a) In-situ DRIFTS of the FeCo&CZA-spent catalyst. **(b)** The optimal reaction pathway for ethanol synthesis on (Fe_{3/4}Co_{1/4})₅C₂(510) surface. Color: C: Gray, H: White, O: Red.

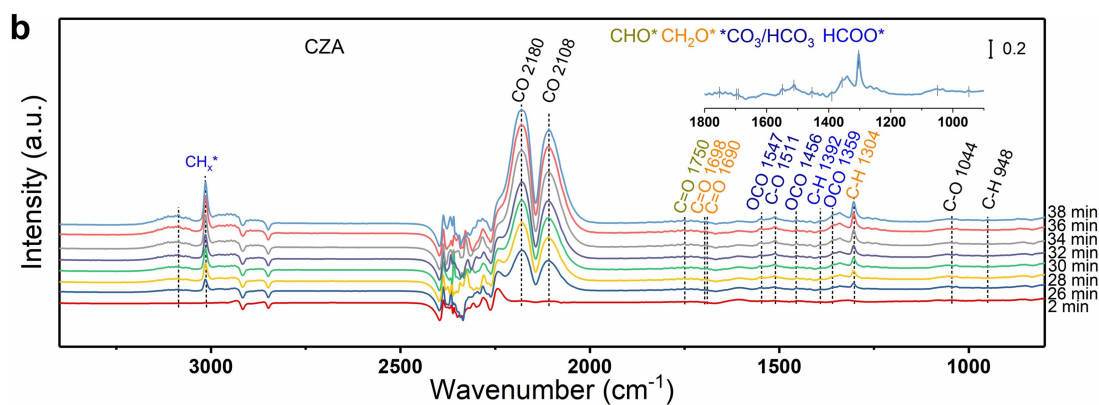
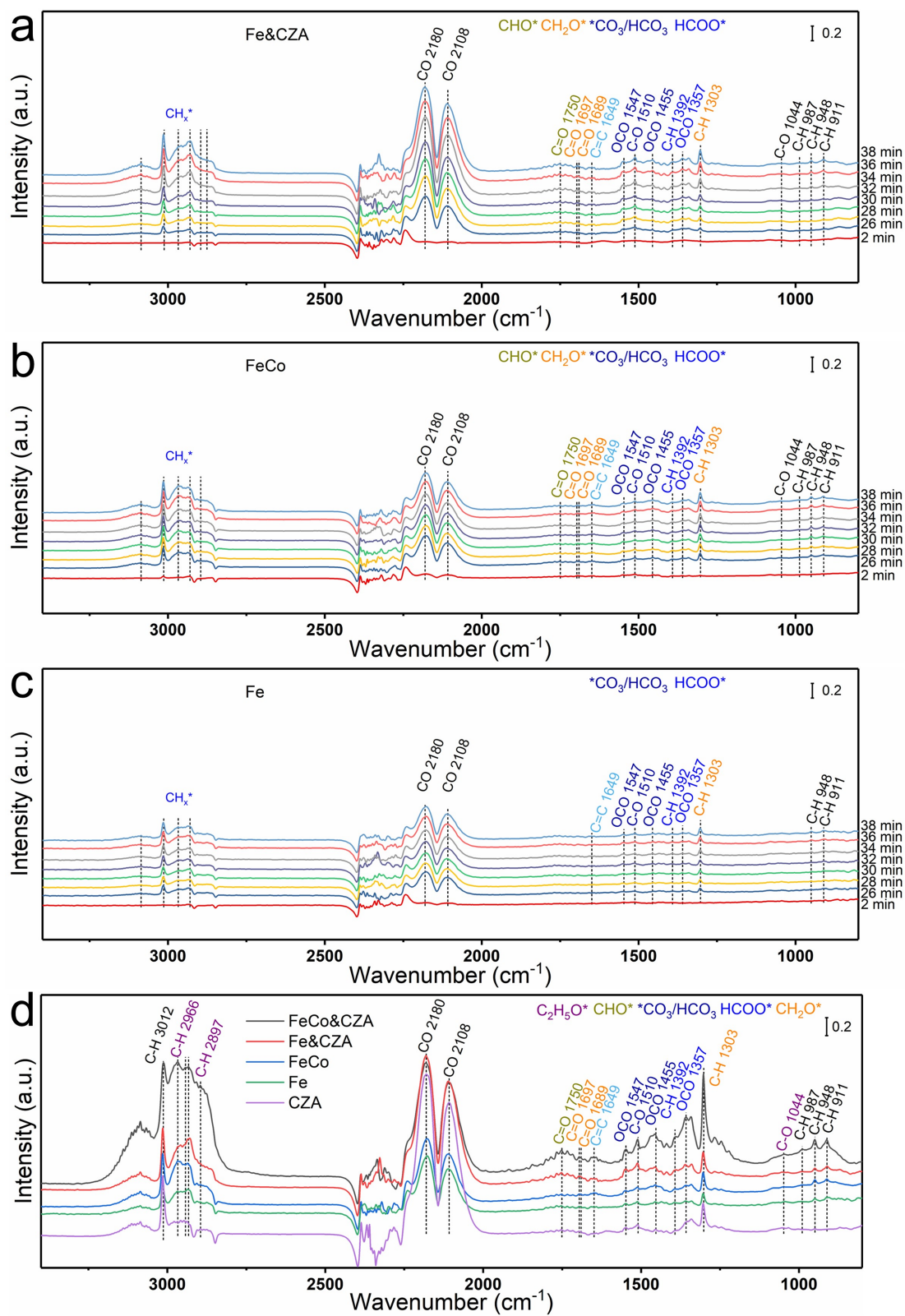


Fig. 4 | (b) In-situ DRIFTS of CZA catalyst.



Supplementary Fig. 28. In-situ DRIFTS of the (a) Fe&CZA, (b) FeCo, (c) Fe catalysts.
(d) In-situ DRIFTS of series catalysts at 38 min.

Reviewer #2 (Remarks to the Author):

Wu et al. developed an excellent FeCo&CZA tandem catalyst for CO₂ hydrogenation to C₂₊ alcohols. Multiple characterization and comprehensive theoretical calculation have thoroughly verified that the controllable oxygen bonding behaviors on the interface of FeCo alloy carbide guarantees the outstanding catalytic performance (high C₂₊ alcohols selectivity of 49.1% at a CO₂ conversion of 51.1%) and long-term stability (>1000 h). The novel and detailed reaction mechanism proposed in this work is promising to shed new light on the rational design of highly efficient C₂₊ alcohols synthesis catalyst. Furthermore, the technical and economic analyses have confirmed the viability of this catalytic system in eliminating carbon emissions at practical application scale. Therefore, I recommend to publish this manuscript after addressing the following issues.

Response: Thanks for the positive comments and invaluable suggestions from reviewer #2. We have polished this work, and the detailed changes have been listed as follows.

1. The influence of reaction conditions (such as temperature and pressure) on the catalytic performance should be investigated in detail.

Response: Thanks for the reviewer's comments. The catalytic performances of the mentioned reference catalysts have been supplemented (**Supplementary Table 5**).

“In addition, we investigated the influence of reaction conditions, such as temperature and pressure, on the catalytic performance of FeCo&CZA (Supplementary Table 5). The CO₂ conversion increased with the increase of temperature from 300 °C to 340 °C and C₂₊OH selectivity increased first and then decreased. As the decrease of pressure from 5MPa to 3MPa, both CO₂ conversion and C₂₊OH selectivity were suppressed, suggesting high pressure promotes the generation of C₂₊OH.”

Supplementary Table 5. The performance of catalysts for CO₂ hydrogenation under different reaction condition.

No.	Temperature (°C)	Pressure (MPa)	X _{CO2}	S _{CO}	S _{H2}	Hydrocarbons				MeO H	C ₂ OH	(Ethanol)	Others	C ₂ OH /ROH(%)	Yield of C ₂ OH (%)	C ₂ OH STY mg g _{cat} ⁻¹ h ⁻¹
						C ₂₋₄	C ₅₊	CH ₄	Paraffin							
1	300	5	41.7	3.4	67.9	13.3	17.3	19.7	17.6	1.2	30.2	23.5	0.7	96.2	12.6	118.3
2	310	5	49.6	2.4	62.6	11.0	17.9	16.7	17.0	0.8	34.8	25.9	1.8	97.8	17.3	163.0
3	340	5	58.4	1.6	71.8	9.1	28.1	15.5	19.1	1.1	24.4	17.3	2.7	95.7	14.2	140.6
4	320	4	50.3	1.8	67.1	11.7	22.7	16.9	15.8	1.3	30.0	21.9	1.6	95.8	15.1	143.4
5	320	3	40.3	4.0	69.4	21.2	12.0	20.8	15.4	1.2	28.5	20.9	0.9	96.0	10.9	106.7

Reaction conditions: FeCo&CZA, 0.2 g, H₂/CO₂ = 3:1, TOS = 8 h, GHSV = 4500 ml⁻¹ g_{cat}⁻¹ h⁻¹.

Other: mainly aldehydes or esters.

$$C_{2+}OH/ROH = \frac{\text{selectivity of } C_{2+}OH}{\text{selectivity of all alcohols}}$$

2. Some new developments reported by other research groups should be updated and included in Figure 1c.

Response: We thank the reviewer for this kind suggestion. The new developments have been supplemented in **Figure 1c** and **Supplementary Table 3**.

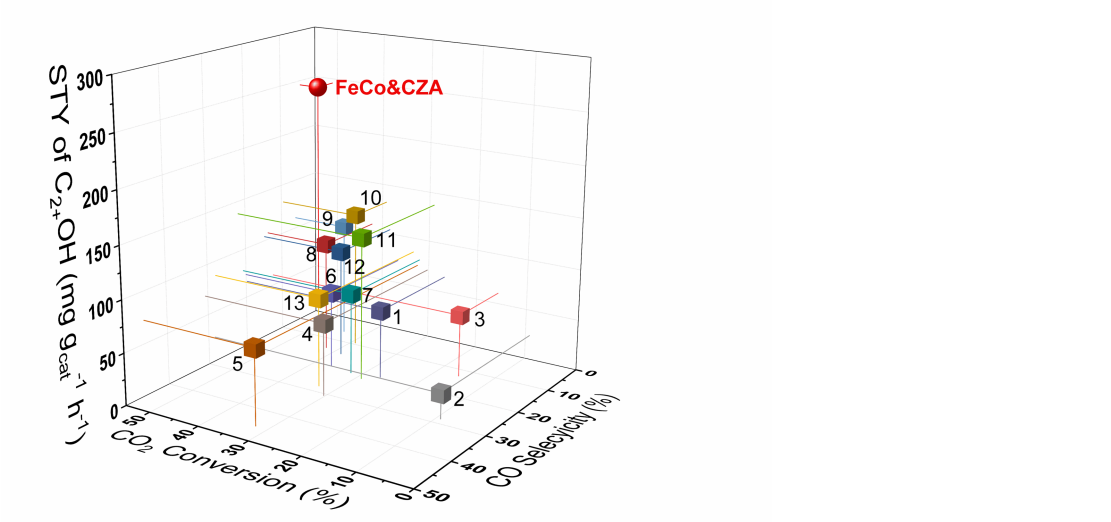


Fig. 1 | Catalytic performance of C₂+OH synthesis from CO₂ hydrogenation. (c) Comparison of CO₂ conversion, CO selectivity, and STY of C₂+OH from FeCo&CZA with the results reported in other literature.

Supplementary Table 3. Comparison of C₂+OH synthesis performance of FeCo&CZA catalyst from CO₂ hydrogenation with other literature reported Fe-based catalysts.

No.	Catalysts	T (°C)	P (MPa)	GHSV (mL g _{cat} ⁻¹ h ⁻¹)	CO ₂ Conv. (%)	CO Sel. (%)	C ₂ +OH Sel. (%)	C ₂ +OH STY (mg g _{cat} ⁻¹ h ⁻¹)	Ref.
1	Rh-Fe/SiO ₂	260	5.0	6000	26.7	19.7	16.0*	65.8*	1
2	Rh-Fe/TiO ₂	270	2.0	8000	9.2	28.4	6.4*	24.2*	2
3	RhFeLi/TiO ₂	250	3.0	6000	15.7	12.5	31.3*	60.5*	3
4	K-CuMgZnFe	320	5.0	6000	30.3	30.6	22.9	69.6	4
5	CZK(1.5)//CFCK(4.5)	350	6.0	5000	32.4	45.3	11.8	72.4	5
6	Cs/Cu-Fe-Zn	330	5.0	4500	36.6	20	19.8	73.4	6
7	FeNaS-0.6	320	3.0	8000	32.0	20.7	12.8	78.5	7
8	K-CuMgZnFe/CZA	320	5.0	6000	42.3	13.8	20.2	106.5	8
9	K/Cu-Zn-Fe	300	7.0	5000	44.2	5.9	19.5*	110.6*	9
10	2%Na-Fe@C/5%K-CuZnAl	320	5.0	4500	39.2	9.4	40.9	132.1*	10
11	ZnFe ₂ O ₄ /Fe-Zn-Na ^a	320	5.0	12000	29.1	21.8	18.6	137.7	11
12	Cr(1%)-CuFe	320	4.0	6000	38.4	14.8	29.2	104.1	12
13	PdFe-6.9 (37 nm)	300	6.0	6000	33.3	27.9	19.1	86.5	13
14	FeCo&CZA	320	5	4500	51.1	4.3	49.1	245.7	This work

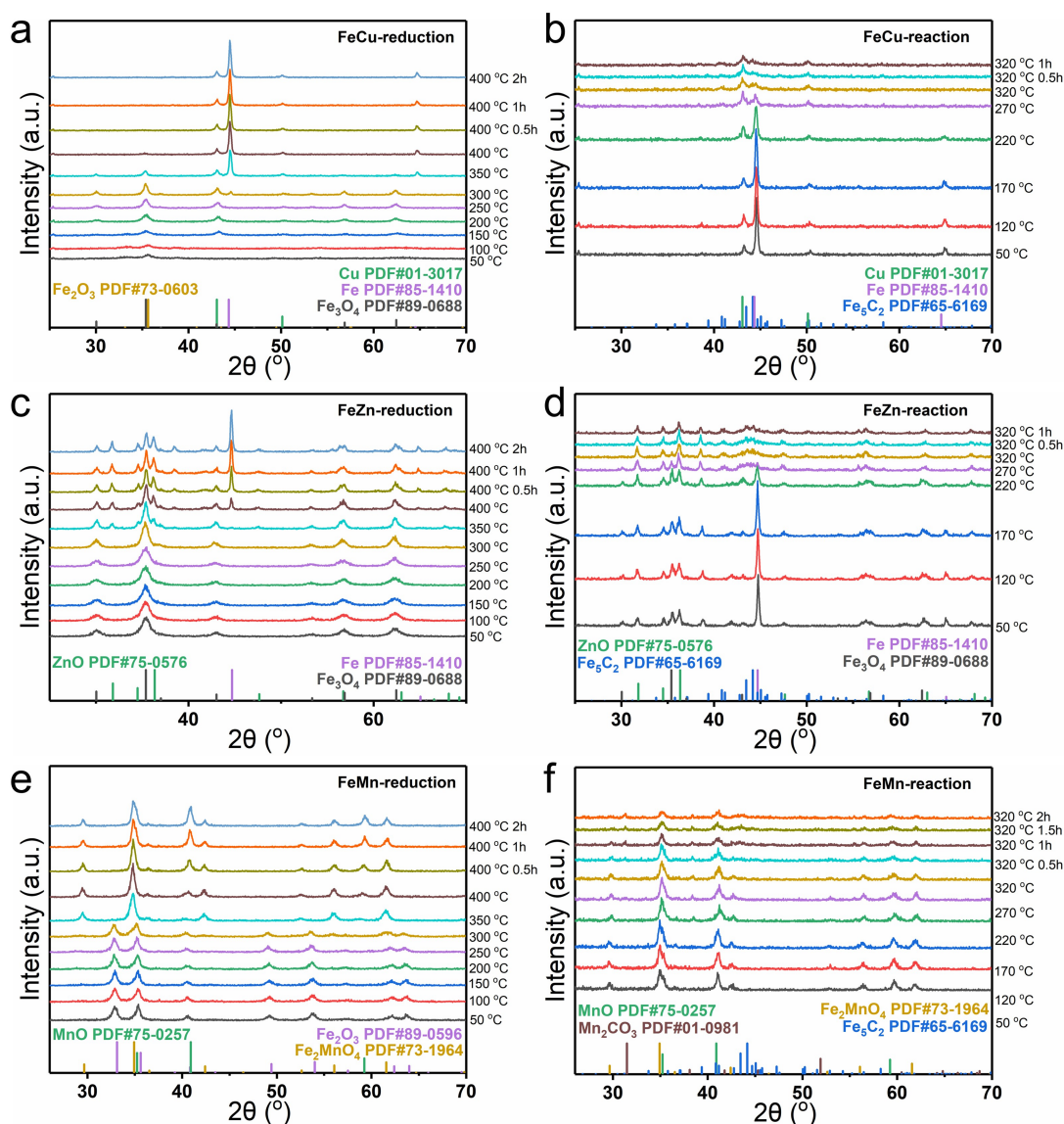
*: only ethanol

3. In supplementary Table 1, other transition metals (Zn/Mn/Cu) were also compounded with Fe-based active site. I wonder that if any alloy carbides were also formed.

Response: Thanks for the reviewer's comment. We supply more evidences by in-situ XRD and XPS for series bimetal FeX catalysts. The supplemented manuscript was as follow:

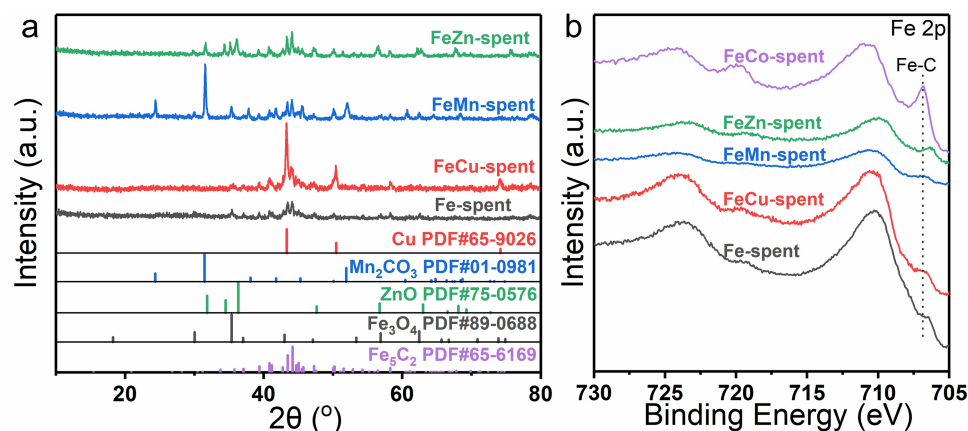
“Other bimetal FeX catalysts are not satisfactory. The phase evolution of bimetal FeX catalysts during reduction and reaction processes was monitored by in-situ XRD

(Supplementary Fig. 1). The phases of Cu, MnCO_3 , ZnO were detected on spent bimetal FeX catalysts, indicating the alloy carbide formed difficultly by these metals (Supplementary Figs. 1 and 2a). As illustrated in Fe2p XPS spectra, the binding energy of Fe-C bond in FeCo alloy carbide was higher than that of other FeX catalysts, suggesting the bonding ability of Fe and C was stronger than those of other FeX catalysts (Supplementary Fig. 2). The formation of FeCo alloy carbides led to lattice stress effect, which affected the electronic structure of Fe atoms.”



Supplementary Fig. 1. The in-situ XRD patterns of (a) FeCu reduction, (b) FeCu reaction, (c) FeZn reduction, (d) FeZn reaction, (e) FeMn reduction, and (f) FeMn

reaction. Reduction conditions: H_2 flow rate of 60 ml min^{-1} . Reaction conditions: 0.8 MPa , $\text{H}_2/\text{CO} = 2$, 80 ml min^{-1} .



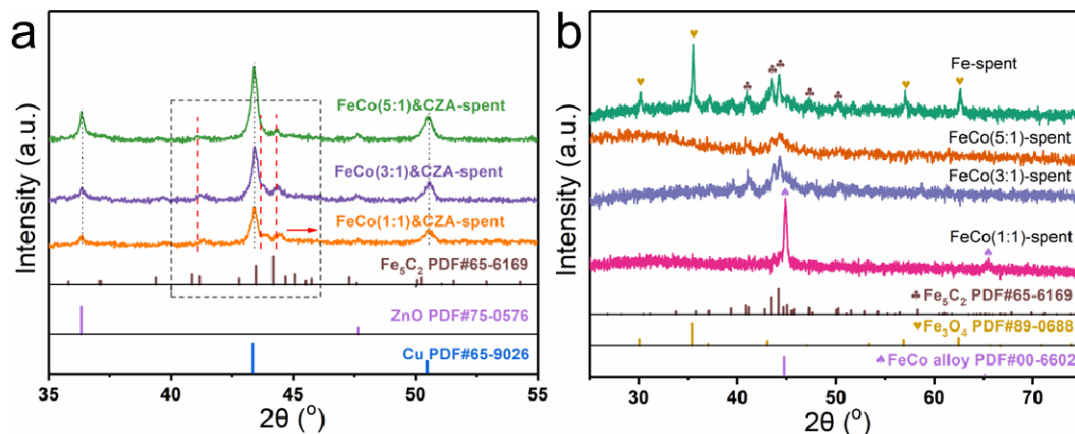
Supplementary Fig. 2. (a) XRD patterns and (b) XPS spectra of series spent catalysts.

4. It is obvious that the Fe/Co ratio is essential for alloy carbide formation, please explain this phenomenon in the main text.

Response: Thanks for the reviewer's comment. The new discussion has been supplemented on **Page 7** in the revised manuscript, as follows:

“Additionally, the carbide diffraction peaks shifted to even higher 2θ angles as the Fe/Co molar ratio decreased (Supplementary Fig. 10a) in FeCo&CZA-spent catalysts, further confirming the enhanced lattice contraction effect. The sole FeCo-spent catalysts with varying Fe/Co ratio were investigated for the process of alloy carbide formation (Supplementary Fig. 10b). For the Fe/Co ratios of 5:1 and 3:1, only the FeCo alloy carbide phase was detected, consistent with the observations for the FeCo&CZA-spent catalysts. However, when the Co content was increased to 50% (Fe/Co = 1:1), both the alloy carbide and FeCo alloy phases were observed in the FeCo(1:1)-spent catalyst. This indicates that an excessive amount of Co is unfavorable for the carburization process. In contrast, the FeCo(1:1)&CZA-spent catalyst exhibited complete carburization of the metallic phase. This suggests that the presence of CZA could significantly promote the carburization of the FeCo alloy, likely due to the generation of carbon-containing species such as CO^ via the reverse water-gas shift*

(RWGS) reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) on CZA component, which can be employed as carburization species.”



Supplementary Fig. 10. XRD patterns of (a) FeCo&CZA-spent catalysts with different ratios of Fe/Co, and (b) Fe-spent catalyst and FeCo-spent catalysts with different ratios of Fe/Co.

5. High quality and comprehensive theoretical calculation is provided in this work, I suggest that the calculation details of $\text{Fe}_5\text{C}_2(510)$ model should be provided in the main text to support the key point of oxygen bonding regulation.

Response: We sincerely thank the reviewer for this valuable suggestion. In response, we have moved the reaction mechanism profile, along with the related discussion of CO_2 hydrogenation on the $\text{Fe}_5\text{C}_2(510)$ surface, into the main text (Figs. 3c and d, Page 13).

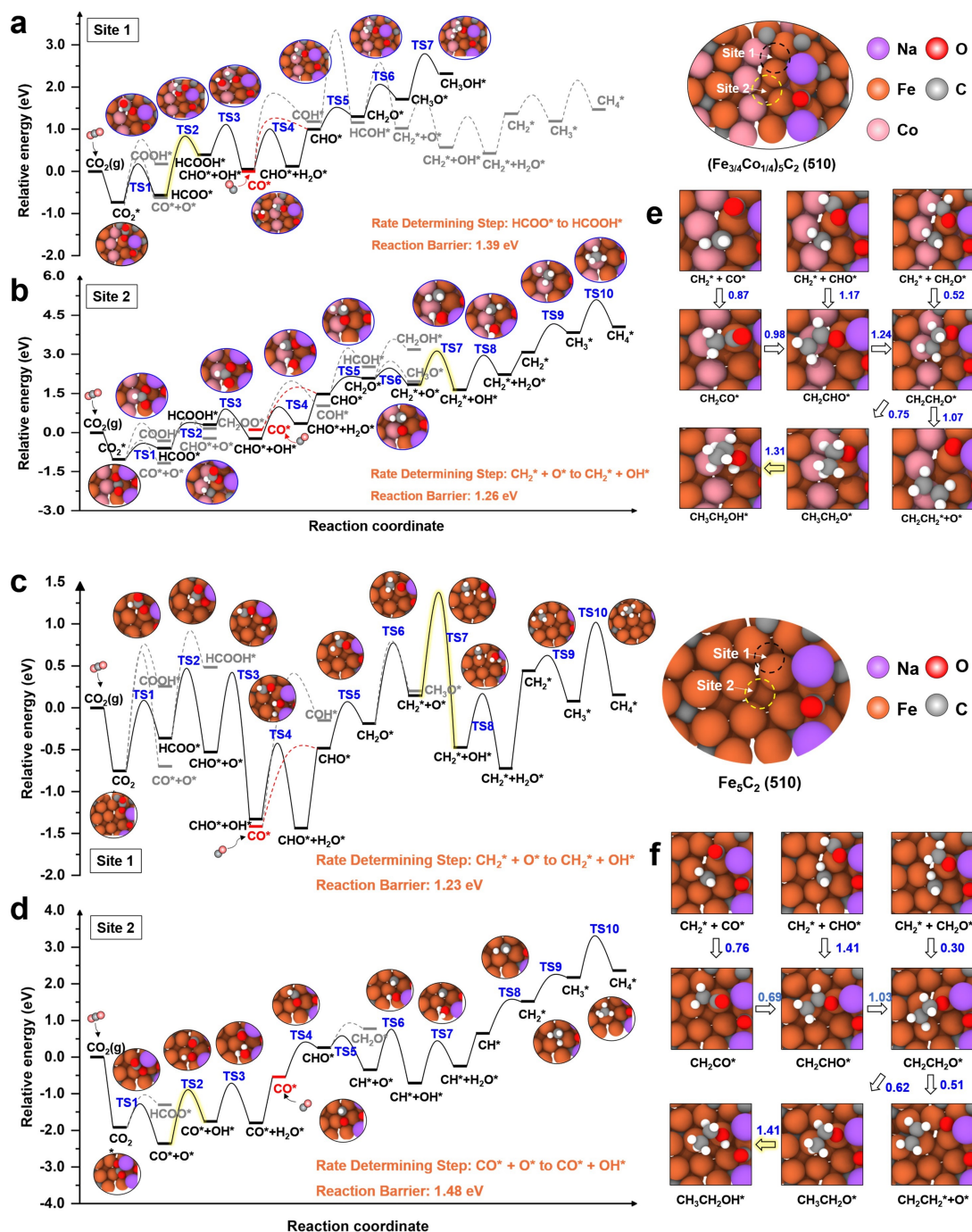


Fig. 3 | The analysis of reaction mechanism of CO_2RR on $(\text{Fe}_{3/4}\text{Co}_{1/4})_5\text{C}_2(510)$ and $\text{Fe}_5\text{C}_2(510)$ surfaces. (a-d) Reaction pathways of CO_2 hydrogenation for C_1 intermediates synthesis on Site 1 and Site 2 of $(\text{Fe}_{3/4}\text{Co}_{1/4})_5\text{C}_2(510)$ and $\text{Fe}_5\text{C}_2(510)$ surfaces. The transition state (TS) in each elementary step is shown as the inset. (e, f) Possible C-C coupling pathways and the corresponding energy barriers on $(\text{Fe}_{3/4}\text{Co}_{1/4})_5\text{C}_2(510)$ and $\text{Fe}_5\text{C}_2(510)$ surfaces.

6. Generally, the FeC_x component can directly dissociate CO to produce CH_x via a carbide mechanism. Has the authors considered this pathway in Fig. 4d?

Response: We thank the referee for raising this important point. Yes, we have considered the possibility of direct CO conversion, since the FeC_x component can indeed facilitate the direct transformation of CO as the referee mentioned. As shown in Figs. 3a and 3b, both $\text{Fe}_5\text{C}_2(510)$ and $(\text{Fe}_{3/4}\text{Co}_{1/4})_5\text{C}_2(510)$ surfaces are capable of converting CO^* into HCO^* , leading to the formation of key intermediates such as CH_2O^* and CH_2^* . The calculated energy barriers for the conversion of CO into CHO^* on the $(\text{Fe}_{3/4}\text{Co}_{1/4})_5\text{C}_2(510)$ surface are 1.20 eV and 1.34 eV at Site 1 and Site 2, respectively, which are slightly higher than those for the direct CO_2 conversion pathway. In contrast, the $\text{Fe}_5\text{C}_2(510)$ surface exhibits lower energy barriers of 0.95 eV and 0.97 eV at Site 1 and Site 2, respectively, making the CO dissociation pathway more favorable than direct CO_2 reduction. These results suggest that $(\text{Fe}_{3/4}\text{Co}_{1/4})_5\text{C}_2(510)$ could promote an alternative pathway that bypasses CO accumulation, thereby facilitating a higher CO_2 conversion. On the other hand, the $\text{Fe}_5\text{C}_2(510)$ surface exhibits inferior performance in CO_2 hydrogenation, and CO produced from iron oxides may instead contribute to the formation of C_{2+} chemicals.

To address this point more clearly, we have added additional discussion in the main text on **Page 14**, as follows:

“What’s more, the formed CO from RWGS process at CZA surface could also be directly used as the reactant to participate in the C_{2+}OH synthesis, and contribute to the improvement of the catalytic performance (Figs. 3a and 3b).”

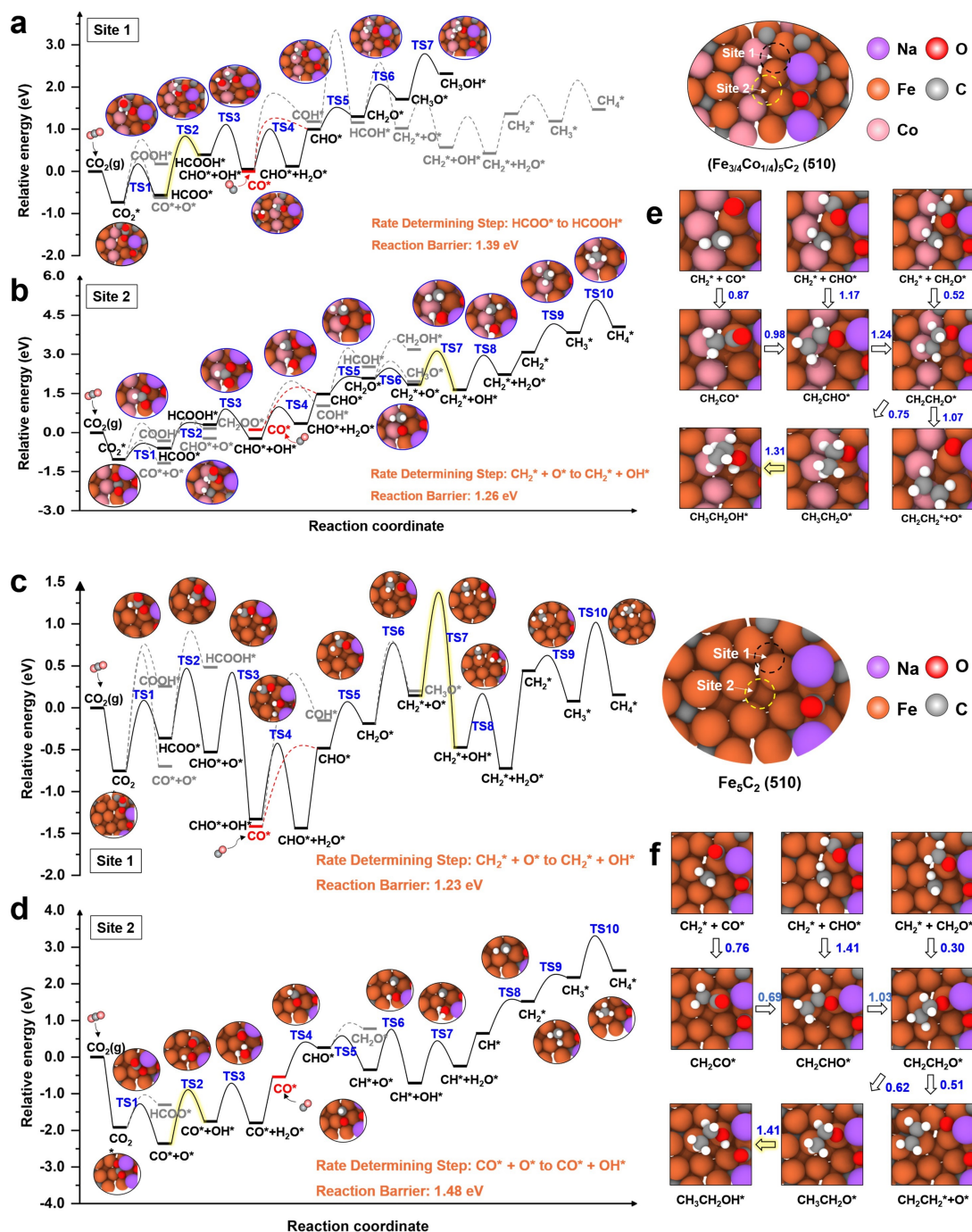


Fig. 3 | The analysis of reaction mechanism of CO_2RR on $(\text{Fe}_{3/4}\text{Co}_{1/4})_5\text{C}_2(510)$ and $\text{Fe}_5\text{C}_2(510)$ surfaces. (a-d) Reaction pathways of CO_2 hydrogenation for C_1 intermediates synthesis on Site 1 and Site 2 of $(\text{Fe}_{3/4}\text{Co}_{1/4})_5\text{C}_2(510)$ and $\text{Fe}_5\text{C}_2(510)$ surfaces. The transition state (TS) in each elementary step is shown as the inset. (e, f) Possible C-C coupling pathways and the corresponding energy barriers on $(\text{Fe}_{3/4}\text{Co}_{1/4})_5\text{C}_2(510)$ and $\text{Fe}_5\text{C}_2(510)$ surfaces.

Reviewer #1 (Remarks to the Author):

This study reports the successful synthesis of high yields of C₂₊ alcohols through CO₂ hydrogenation using a combination of FeCo alloy and a copper/zinc/aluminum (CZA) catalyst. The FeCo&CZA catalyst system achieved a 51.1% CO₂ conversion and a 49.1% selectivity towards C₂₊ alcohols at a reaction temperature of 320°C and a pressure of 5 MPa. The catalyst demonstrated excellent stability, maintaining performance for over 1000 hours of continuous operation. Additionally, the reaction mechanism was investigated using density functional theory (DFT) and other analytical methods. Economic evaluations of the process were also conducted.

The authors addressed well the issues I raised in my initial review report, but I can see there are still a few issues that have to be further addressed before the final acceptance:

Response: We sincerely thank the reviewer for their insightful comments and valuable suggestions, which have greatly helped us improve the quality of our manuscript. In response to the reviewer's feedback, we have revised our manuscript carefully, and the detailed changes are summarized as follows.

1. The role of Co needs to be more clearly explained. The authors state that the incorporation of other metals along with Fe promotes the formation of the carbide phase, as evidenced by in-situ XRD and XPS analyses. However, the underlying mechanism by which Co specifically facilitates the formation of the carbide phase has not been sufficiently analyzed or discussed. A more detailed explanation, supported by appropriate references, is necessary to clarify the effect of Co.

Response: Thanks for the reviewer's comment. This is of great value in improving the clarity and readability of the manuscript. In response, we have cited a more appropriate reference and revised the relevant sections accordingly. The specific improvements are summarized below:

(1) The role of Co has been explained in Introduction section as follow (Pages 3-4):

“Cobalt (Co) is well-known for its excellent catalytic activity in CO/CO₂ hydrogenation

reactions^{22,24,28,29}. Unlike iron (Fe), which tends to partially convert to Fe₃O₄ during CO₂ hydrogenation, cobalt and cobalt carbide (e.g., Co₂C) remains predominantly, having a lower oxygen affinity for Co compared to Fe^{18,30-34}. This makes cobalt and cobalt carbide active for non-dissociative CO adsorption and subsequent insertion processes in the Co/Co₂C catalysts^{25,35,36}. Lee et al. reported that a FeCo alloy carbide phase could be formed from a FeCo alloy during the CO₂ hydrogenation reaction at 340 °C³⁷. Ma et al. developed CoFe bimetallic carbide catalysts derived from Co/ α -Fe₂O₃ nanorods through interdiffusion of Co and Fe species during the reduction process, where Co atoms replace Fe atoms to form FeCo alloy carbides under reaction conditions²². Furthermore, they synthesized a monodisperse ϵ' -(Co_xFe_{1-x})_{2.2}C alloy carbide catalyst, which is obtained from Co_xFe_{3-x}O₄ spinel oxide nanoparticles as precursors³⁸. Zhong et al. demonstrated that Co atoms can be uniformly distributed and doped into Fe₂C, leading to the formation of (Fe_xCo_y)₂C alloy carbide²⁴. Guo et al. further reported that Co atoms readily incorporate into the iron carbide when the precursors contain Co and Fe species in close proximity. By tuning the carburization time and temperature, specific CoFe alloy carbides with controlled composition and structure were successfully obtained³⁹.”

“Therefore, the presence of Co offers a unique advantage by promoting the formation of Fe-based alloy carbides, thereby enhancing its catalytic performance in CO₂ hydrogenation to C₂+OH products.”

“Therefore, the elements Fe and Co readily form alloy carbide, which can be attributed to their adjacent atomic numbers and similar chemical properties. Further evidence and analysis will be provided in the following discussion. Unlike previous studies on FeCo alloy carbides^{28,39}, our work demonstrates the exceptional long-term stability of the designed catalyst over 1000 hours, as well as its distinct oxygen-binding capability. More importantly, we elucidate the underlying mechanism of CO₂ conversion to C₂+OH products in a clear and intuitive manner. To the best of our knowledge, this is the first report of Co-stabilized alloy carbides that enable efficient CO₂ hydrogenation to C₂+OH.”

Reference:

- 18 Zhong, L.; Yu, F.; An, Y.; Zhao, Y.; Sun, Y.; Li, Z.; Lin, T.; Lin, Y.; Qi, X.; Dai, Y.; Gu, L.; Hu, J.; Jin, S.; Shen, Q. & Wang, H. Cobalt carbide nanoprisms for direct production of lower olefins from syngas. *Nature* 538, 84-87, (2016) doi:10.1038/nature19786.
- 22 Zeng, Z.; Li, Z.; Guan, T.; Guo, S.; Hu, Z.; Wang, J.; Rykov, A.; Lv, J.; Huang, S.; Wang, Y. & Ma, X. CoFe alloy carbide catalysts for higher alcohols synthesis from syngas: Evolution of active sites and Na promoting effect. *J. Catal.* 405, 430-444, (2022) doi:10.1016/j.jcat.2021.12.024.
- 24 Gong, K.; Wei, Y.; Lin, T.; Qi, X.; Sun, F.; Jiang, Z. & Zhong, L. Maximizing the interface of dual active sites to enhance higher oxygenate synthesis from syngas with high activity. *ACS Catal.* 13, 4533-4543, (2023) doi:10.1021/acscatal.3c00363.
- 25 Zhang, S.; Huang, C.; Shao, Z.; Zhou, H.; Chen, J.; Li, L.; Lu, J.; Liu, X.; Luo, H.; Xia, L.; Wang, H. & Sun, Y. Revealing and regulating the complex reaction mechanism of CO₂ hydrogenation to higher alcohols on multifunctional tandem catalysts. *ACS Catal.* 13, 3055-3065, (2023) doi:10.1021/acscatal.2c06245.
- 28 Liu, N.; Wei, J.; Xu, J.; Yu, Y.; Yu, J.; Han, Y.; Wang, K.; Orege, J. I.; Ge, Q. & Sun, J. Elucidating the structural evolution of highly efficient Co-Fe bimetallic catalysts for the hydrogenation of CO₂ into olefins. *Appl. Catal. B: Environ.* 328, 122476, (2023) doi:10.1016/j.apcatb.2023.122476.
- 29 Zhang, L.; Dang, Y.; Zhou, X.; Gao, P.; Petrus van Bavel, A.; Wang, H.; Li, S.; Shi, L.; Yang, Y.; Vovk, E. I.; Gao, Y. & Sun, Y. Direct conversion of CO₂ to a jet fuel over CoFe alloy catalysts. *Innovation* 2, 100170, (2021) doi:10.1016/j.xinn.2021.100170.
- 30 Zhang, S.; Liu, X.; Shao, Z.; Wang, H. & Sun, Y. Direct CO₂ hydrogenation to ethanol over supported Co₂C catalysts: Studies on support effects and mechanism. *J. Catal.* 382, 86-96, (2020) doi:10.1016/j.jcat.2019.11.038.

- 31 Zhu, J.; Wang, P.; Zhang, X.; Zhang, G.; Li, R.; Li, W.; Senftle, T. P.; Liu, W.; Wang, J.; Wang, Y.; Zhang, A.; Fu, Q.; Song, C. & Guo, X. Dynamic structural evolution of iron catalysts involving competitive oxidation and carburization during CO₂ hydrogenation. *Sci. Adv.* 8, eabm3629, (2022) doi:10.1126/sciadv.abm3629.
- 32 Wang, M.; Wang, P.; Zhang, G.; Cheng, Z.; Zhang, M.; Liu, Y.; Li, R.; Zhu, J.; Wang, J.; Bian, K.; Liu, Y.; Ding, F.; Senftle, T. P.; Nie, X.; Fu, Q.; Song, C. & Guo, X. Stabilizing Co₂C with H₂O and K promoter for CO₂ hydrogenation to C₂+ hydrocarbons. *Sci. Adv.* 9, eadg0167, (2023) doi:10.1126/sciadv.adg0167.
- 33 Sun, F.; Yang, R.; Xia, Z.; Yang, Y.; Zhao, Z.; Gu, S.; Wu, D.; Ding, Y. & Jiang, Z. Effects of cobalt carbide on Fischer–Tropsch synthesis with MnO supported Co-based catalysts. *J. Energy Chem.* 42, 227-232, (2020) doi:10.1016/j.jechem.2019.07.007.
- 34 Chai, B.; Huang, C.; Li, S.; Yang, M.; Xiao, H. & Fang, K. Highly selective syngas conversion to higher oxygenates over CuZnAl|CoFe multifunctional catalysts. *Int. J. Hydrogen Energy* 110, 168–180, (2024) doi:10.1016/j.ijhydene.2025.02.227.
- 35 Zhang, R.; Wen, G.; Adidharma, H.; Russell, A. G.; Wang, B.; Radosz, M. & Fan, M. C₂ oxygenate synthesis via Fischer–Tropsch synthesis on Co₂C and Co/Co₂C interface catalysts: How to control the catalyst crystal facet for optimal selectivity. *ACS Catal.* 7, 8285-8295, (2017) doi:10.1021/acscatal.7b02800.
- 36 Zhao, Z.; Lu, W.; Yang, R.; Zhu, H.; Dong, W.; Sun, F.; Jiang, Z.; Lyu, Y.; Liu, T.; Du, H. & Ding, Y. Insight into the formation of Co@Co₂C catalysts for direct synthesis of higher alcohols and olefins from syngas. *ACS Catal.* 8, 228-241, (2018) doi:10.1021/acscatal.7b02403.
- 37 Kim, K. Y.; Lee, H.; Noh, W. Y.; Shin, J.; Han, S. J.; Kim, S. K.; An, K. & Lee, J. S. Cobalt ferrite nanoparticles to form a catalytic Co-Fe alloy carbide phase for selective CO₂ hydrogenation to light olefins. *ACS Catal.* 10, 8660-8671, (2020) doi:10.1021/acscatal.0c01417.
- 38 Zeng, Z.; Li, Z.; Kang, L.; Han, X.; Qi, Z.; Guo, S.; Wang, J.; Rykov, A.; Lv, J.; Wang, Y. & Ma, X. A monodisperse ε'-(Co_xFe_{1-x})_{2.2}C bimetallic carbide catalyst

for direct conversion of syngas to higher alcohols. ACS Catal. 12, 6016-6028, (2022) doi:10.1021/acscatal.2c01078.

- 39 *Liu, N.; Fan, Q.; Wei, J.; Zhang, G.; Sun, J.; Li, W.; Song, C. & Guo, X. Fine-tuning the active phases of CoFe alloy carbides for boosting olefin synthesis from CO₂ hydrogenation. ACS Catal. 15, 179-192, (2025) doi:10.1021/acscatal.4c06112.*

(2) Detailed evidence and analysis of the FeCo alloy carbide are provided in the section “Confirmation of FeCo alloy carbide”, as summarized below:

Compared to the spent Fe&CZA (Fe&CZA-spent) catalyst, where χ -Fe₅C₂ is the dominant carbide phase, the FeCo&CZA-spent catalyst retained prominent diffraction peaks corresponding to the carbide phase. Notably, these peaks shifted to higher 2 θ angles without the appearance of any new diffraction peaks (Fig. 2a), indicating a lattice contraction effect, likely caused by Co incorporation into the Fe carbide structure.

In addition, the H₂-temperature programmed reduction (TPR), CO-temperature programmed desorption (TPD) (Supplementary Fig. 11) and N₂ adsorption-desorption isotherm (Supplementary Fig. 12, Supplementary Table 7) further verified the structural evolution of the catalysts. In H₂-TPR, the Fe catalyst underwent stepwise reduction from the initial α -Fe₂O₃ to Fe₃O₄, FeO, and finally to metallic Fe. In contrast, the FeCo catalyst exhibited a distinct reduction peak corresponding to the transformation of the FeCo alloy oxide phase into the FeCo alloy. Notably, the reduction peaks shifted toward lower temperatures upon Co addition, suggesting that the Co facilitates the reduction of the FeCo catalysts. The carburization behaviors of catalyst were monitored by CO-TPD, the desorption peaks obviously shifted toward the higher temperature, indicating that the carburization of FeCo metallic phase is difficult than that of Fe catalyst, corresponding to the results of XRD (Supplementary Fig. 10b). Nitrogen physisorption analysis revealed that the FeCo catalyst possessed a larger specific surface area and a predominantly mesoporous structure compared to the Fe catalyst. After the reaction, the surface area of FeCo-spent and Fe-spent became comparable. Taken together, it is

reasonable to speculate the formation of FeCo alloy carbide phase.

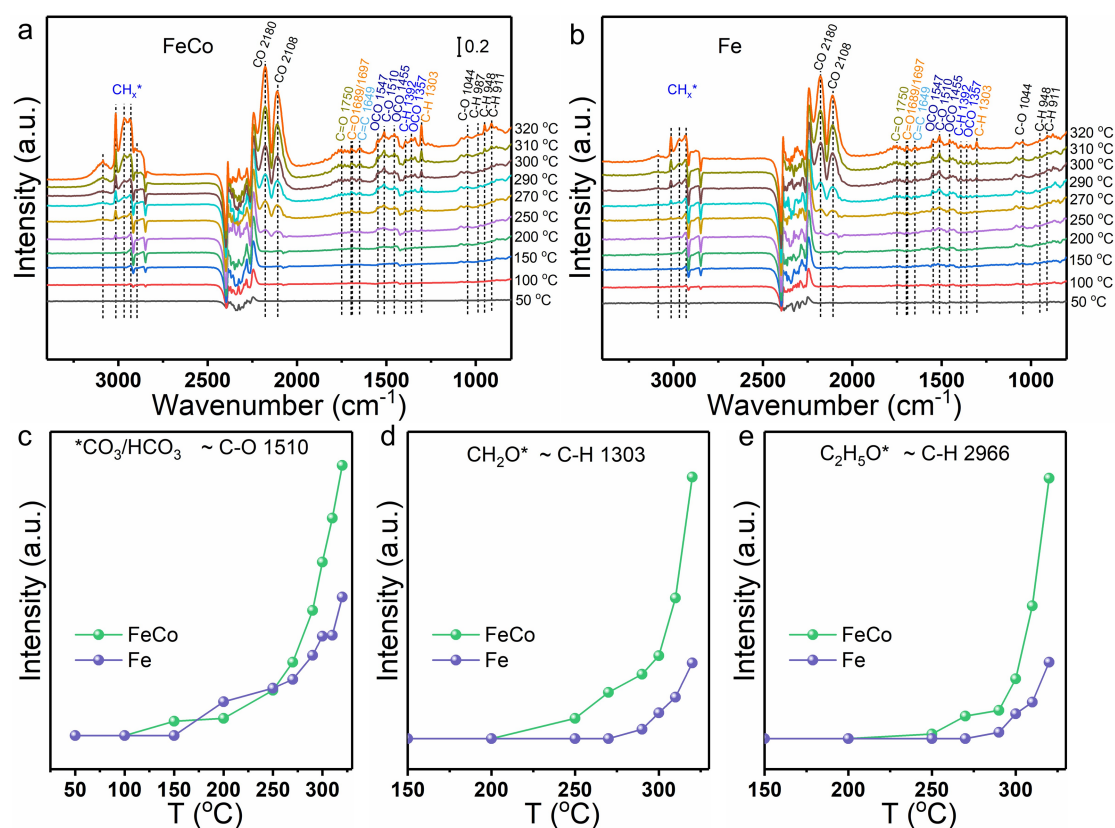
To verify the above speculation, we next used the $(\text{Fe}_{3/4}\text{Co}_{1/4})_5\text{C}_2$ with an Fe/Co molar ratio of 3 as a model system and performed density functional theory (DFT) computations to identify the most thermodynamically stable configuration from the broad compositional space of FeCo alloy carbide (Supplementary Fig. 13). Radical distribution function (RDF) analysis confirmed that the lattice contraction observed in the FeCo alloy carbide originated from a shortened Fe–C bond length upon Co incorporation. The simulated XRD pattern of $(\text{Fe}_{3/4}\text{Co}_{1/4})_5\text{C}_2$ showed diffraction peaks shifted to higher angles compared to Fe_5C_2 (Supplementary Fig. 14), consistent with the experimental XRD results of Fe&CZA-spent and FeCo&CZA-spent catalysts (Fig. 2a). Further extended X-ray absorption fine structure (EXAFS) analysis provided coordination information for Fe and Co species. The Fe–C bond length in FeCo&CZA-spent (1.98 Å) was shorter than that in Fe&CZA-spent (2.08 Å) (Fig. 2b; Supplementary Fig. 15; Supplementary Tables 8 and 9), in good agreement with the RDF results. Additionally, aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) and the corresponding energy-dispersive X-ray (EDX) mapping revealed a uniform distribution of Fe, Co, and C elements in the spent catalyst (Fig. 2c).

The phase evolution of the FeCo&CZA catalyst was further investigated using in situ X-ray diffraction (XRD) (Supplementary Fig. 16). During the H_2 reduction process, the FeCo alloy oxide was first converted into a metallic FeCo alloy. Subsequently, FeCo alloy carbide formed during the CO_2 hydrogenation step, driven by the carburization of the FeCo alloy through CO generated via the reverse water-gas shift (RWGS) reaction (Fig. 2d). Therefore, based on the combined results from multiple characterization techniques and DFT simulations, it is reasonable to conclude that the FeCo&CZA-spent catalyst contains a FeCo alloy carbide phase, rather than separate Fe- or Co-based carbides. Co facilitated the formation of FeCo alloy carbide phase for CO_2 hydrogenation to C_2+OH .

2. The comparison between FeCo and Fe catalysts in the in-situ DRIFTS results needs to be more convincing. Although the authors discuss the role of Co based on differences observed in the fingerprint region (Fig. S26), it is difficult to clearly distinguish such differences from the data presented. The distinctions between the two catalysts must be shown more explicitly in order for the authors' claims regarding Co's effect to be convincing.

Response: Thanks for the reviewer's comment. In response, we have carefully addressed the comparison between the FeCo and Fe catalysts, as revealed by *in-situ* DRIFTS at various temperatures. The detailed spectral changes are discussed in the manuscript as follows:

In the fingerprint region (1200~1900 cm⁻¹), the FeCo catalyst exhibited more abundant characteristic peaks than the Fe catalyst (Supplementary Fig. 27), indicating a richer variety of surface intermediates. The peaks corresponding to carbonate species (CO₃ and HCO₃*) with typical bands at 1510 cm⁻¹ appeared as early as 150 °C, and their intensities increased progressively with temperature on both catalysts. However, the C-H stretching peak of the CH₂O* (~1303 cm⁻¹) emerged at 250 °C for the FeCo catalyst, while it appeared later, at 290 °C, for the Fe catalyst. The FeCo catalyst also exhibited stronger signal intensity. A similar trend was observed for the C-H vibration of the C₂H₅O* species (~2966 cm⁻¹) further confirming the enhanced activity. Therefore, the introduction of Co could promote the formation of O-containing intermediates, which can be attributed to the effect of Site 1 (Fig. 3a) on the surface of FeCo alloy carbide.*



Supplementary Fig. 27. In-situ DRIFTS of (a) FeCo and (b) Fe at different temperature. (c-e) The peaks intensity on in-situ DRIFTS in FeCo and Fe catalysts at series temperature.

3. While the authors make various claims based on their experimental results, these claims should be supported by relevant references to enhance their clarity and credibility. The addition of supporting literature would help solidify the arguments presented.

Response: Thanks for the reviewer's comment. The references about the role of Co on introduction section has been supplemented, as shown in Question 1. In addition, we also cited the relevant references to support our experimental results as follow:

Page 2-3

In particular, thermal-catalytic hydrogenation of CO₂ coupled with sustainable water photo/electrolysis H₂ is attracting more and more attention due to its integrated advantages of industrial applicability, greenhouse effect elimination, and non-fossil fuel-based product synthesis⁶⁻¹¹.

10 Garg, S.; Xie, Z. & Chen, J. G. Tandem reactors and reactions for CO₂ conversion.

Nat. Chem. Eng. **1**, 139-148, (2024) doi:10.1038/s44286-023-00020-2.

- 11 Ye, J.; Dimitratos, N.; Rossi, L. M.; Thonemann, N.; Beale, A. M. & Wojcieszak, R. Hydrogenation of CO₂ for sustainable fuel and chemical production. *Science* **387**, eadn9388, (2025) doi:10.1126/science.adn9388.

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Additionally, the carbide diffraction peaks shifted to even higher 2θ angles as the Fe/Co molar ratio decreased (Supplementary Fig. 10a) in FeCo&CZA-spent catalysts^{51,52}, further confirming the enhanced lattice contraction effect.

- 51 Gnanamani, M. K.; Jacobs, G.; Hamdeh, H. H.; Shafer, W. D.; Liu, F.; Hopps, S. D.; Thomas, G. A. & Davis, B. H. Hydrogenation of carbon dioxide over Co-Fe bimetallic catalysts. *ACS Catal.* **6**, 913-927, (2016) doi:10.1021/acscatal.5b01346.
- 52 Xu, F.; Yang, D.; Jin, D.; Meng, X.; Zhao, R.; Dai, W. & Xin, Z. MOFs-derived Fe-Co bimetallic catalyst for selective CO₂ hydrogenation to light olefins. *Ind. Eng. Chem. Res.* **63**, 20800-20811, (2024) doi:10.1021/acs.iecr.4c02853.

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This suggests that the presence of CZA could significantly promote the carburization of the FeCo alloy²⁶, likely due to the generation of carbon-containing species such as CO* via the reverse water-gas shift (RWGS) reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) on CZA component, which can be employed as carburization species.

- 26 Wang, Y.; Wang, K.; Zhang, B.; Peng, X.; Gao, X.; Yang, G.; Hu, H.; Wu, M. & Tsubaki, N. Direct conversion of CO₂ to ethanol boosted by intimacy-sensitive multifunctional catalysts. *ACS Catal.* **11**, 11742-11753, (2021) doi:10.1021/acscatal.1c01504.

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Notably, the reduction peaks shifted toward lower temperatures upon Co addition²⁸, suggesting that the Co facilitates the reduction of the FeCo catalysts.

- 28 Liu, N.; Wei, J.; Xu, J.; Yu, Y.; Yu, J.; Han, Y.; Wang, K.; Orege, J. I.; Ge, Q. & Sun, J. Elucidating the structural evolution of highly efficient Co-Fe bimetallic catalysts for the hydrogenation of CO₂ into olefins. *Appl. Catal. B: Environ.* **328**, 122476, (2023) doi:10.1016/j.apcatb.2023.122476.

Page 9

The carburization behaviors of catalyst were monitored by CO-TPD, the desorption peaks obviously shifted toward the higher temperature²², indicating that the carburization of FeCo metallic phase is difficult than that of Fe catalyst, corresponding to the results of XRD (Supplementary Fig. 10b).

- 22 Zeng, Z.; Li, Z.; Guan, T.; Guo, S.; Hu, Z.; Wang, J.; Rykov, A.; Lv, J.; Huang, S.; Wang, Y. & Ma, X. CoFe alloy carbide catalysts for higher alcohols synthesis from syngas: Evolution of active sites and Na promoting effect. *J. Catal.* **405**, 430-444, (2022) doi:10.1016/j.jcat.2021.12.024.

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This hypothesis was then supported by temperature-programmed oxidation-mass spectrometry (TPO-MS, Fig. 2e) and in-situ water oxidation XRD results (Supplementary Fig. 17), where FeCo alloy carbide showed robust stability than the monometallic Fe carbide (Fe₅C₂) under the water oxidation conditions⁵³⁻⁵⁵.

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Meanwhile, water contact angles test demonstrated an enhanced hydrophobicity of the FeCo alloy carbide compared to the Fe carbide^{17,56} (Supplementary Fig. 17).

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Reviewer #2 (Remarks to the Author):

The revised manuscript is satisfactory to me and can be published.

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