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## Ethanol synthesis *via* catalytic CO<sub>2</sub> hydrogenation over multi-elemental KFeCuZn/ZrO<sub>2</sub> catalyst†

Pengfei Du,<sup>a</sup> Abdellah Ait El Fakir,<sup>\*a</sup> Shirun Zhao,<sup>a</sup> Nazmul Hasan M. D. Dostagir,<sup>id a</sup> HongLi Pan,<sup>a</sup> Kah Wei Ting,<sup>a</sup> Shinya Mine,<sup>id b</sup> Yucheng Qian,<sup>a</sup> Ken-ichi Shimizu<sup>id \*a</sup> and Takashi Toyao<sup>id \*a</sup>

Technological enablers that use CO<sub>2</sub> as a feedstock to create value-added chemicals, including ethanol, have gained widespread appeal. They offer a potential solution to climate change and promote the development of a circular economy. However, the conversion of CO<sub>2</sub> to ethanol poses significant challenges, not only because CO<sub>2</sub> is a thermodynamically stable and chemically inert molecule but also because of the complexity of the reaction routes and uncontrollability of C–C coupling. In this study, we developed an efficient catalyst, K–Fe–Cu–Zn/ZrO<sub>2</sub> (KFeCuZn/ZrO<sub>2</sub>), which enhances the EtOH space time yield (STY<sub>EtOH</sub>) to 5.4 mmol g<sub>cat</sub><sup>−1</sup> h<sup>−1</sup>, under optimized conditions (360 °C, 4 MPa, and 12 L g<sub>cat</sub><sup>−1</sup> h<sup>−1</sup>). Furthermore, we investigated the roles of each constituent element using *in situ/operando* spectroscopy such as X-ray absorption spectroscopy (XAS) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). These results demonstrate that all components are necessary for efficient ethanol synthesis.

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## Introduction

CO<sub>2</sub> hydrogenation into chemicals and fuels is recognized as a pivotal process for achieving a sustainable carbon cycle.<sup>1–4</sup> The CO<sub>2</sub> hydrogenation into C<sub>2+</sub> alcohols has great industrial significance but is scientifically challenging, primarily because of the intricate reaction mechanisms involved and necessity of forming carbon–carbon (C–C) bonds, resulting in the low selectivity of C<sub>2+</sub> alcohols.<sup>5–8</sup> Among the various C<sub>2+</sub> alcohol products,<sup>6,7</sup> ethanol (EtOH) has received widespread attention in recent years as an alternative fuel,<sup>9–11</sup> promising hydrogen carrier,<sup>9,12</sup> and versatile building block chemical for producing high-value products.<sup>9,13–15</sup> EtOH generation not only involves competition from several parallel reactions, including the formation of C<sub>2+</sub> hydrocarbons and methanol, but also requires precise control of the dissociative and non-dissociative activation of C–O bonds to obtain surface alkyl and CO (H) species, respectively.<sup>5,6,12,16</sup> Therefore, achieving high selectivity and yield toward EtOH is challenging but urgently desired for future CO<sub>2</sub> utilization.<sup>5,9,13,14</sup>

Various catalytic systems have been reported for the hydrogenation of CO<sub>2</sub> into EtOH. Among these catalytic

materials, noble-metal-based catalysts (Pd<sup>17–20</sup> and Rh<sup>21–25</sup>) are usually applied to promote C–O activation and the subsequent C–C coupling for EtOH synthesis.<sup>7,13</sup> The high price of noble metal catalysts limits their further application; thus, researchers have shifted their attention to 3d transition metal catalysts, such as Cu,<sup>19,26–29</sup> Fe,<sup>30–34</sup> and Co<sup>4,35–38</sup>-based catalysts, coupled with promoter elements such as alkali metal oxides. Among the 3d transition metal catalysts, Fe–Cu catalysts stand out as a cost-effective option with exceptional catalytic activity to produce C<sub>2+</sub> alcohols from CO<sub>2</sub>.<sup>30,32,39</sup> However, they also generate a substantial amount of hydrocarbons as byproducts.<sup>32,39,40</sup> Although some recent work has suggested that the introduction of Zn into Cs-promoted Fe–Cu based catalysts would be more efficient in producing EtOH,<sup>30</sup> the catalytic performance does not meet industrial requirements. In addition, little is known about the role of each element. Further improvements in the catalyst systems are essential for developing industrially valuable reaction processes.

Herein, we present a highly efficient catalytic system, namely K-promoted FeCuZn/ZrO<sub>2</sub> (KFeCuZn/ZrO<sub>2</sub>), which significantly enhances the rate of EtOH production through CO<sub>2</sub> hydrogenation. Under optimized conditions (360 °C, 4 MPa, and 12 L g<sub>cat</sub><sup>−1</sup> h<sup>−1</sup>), our catalyst (KFeCuZn/ZrO<sub>2</sub>) exhibits high activity (STY<sub>EtOH</sub>: 5.4 mmol g<sub>cat</sub><sup>−1</sup> h<sup>−1</sup>) in the EtOH synthesis, compared to different supports. We thoroughly investigated the role of each constituent element using *in situ/operando* spectroscopic techniques and various characterizations.

<sup>a</sup>Institute for Catalysis, Hokkaido University, Sapporo 001-0021, Japan. E-mail: toyao@cat.hokudai.ac.jp; Abdellah@cat.hokudai.ac.jp; kshimizu@cat.hokudai.ac.jp

<sup>b</sup>National Institute of Advanced Industrial Science and Technology (AIST), Research Institute for Chemical Process Technology, 4-2-1 Nigatake, Miyagino, Sendai 983-8551, Japan

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## Experimental details

### Chemicals and catalyst preparation

Chemicals and materials were purchased from commercial suppliers and used without further purification. ZrO<sub>2</sub> (RC-100), equivalent to JRC-ZRO-3, was supplied by Daiichi Kigenso Kagaku Kogyo. TiO<sub>2</sub> (P25) was obtained from Evonik.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Puralox) was obtained from Sasol. SiO<sub>2</sub> (CariACT Q-10) was purchased from Fuji Silysia Chemical Company, Ltd.

KFeCuZn/support catalysts were prepared using a simple impregnation method. In this process, the support material was impregnated with an aqueous solution of KNO<sub>3</sub> (>98%; Wako Pure Chemical Industries), Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (>98%; Wako Pure Chemical Industries), Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (>98%; Kanto Chemical), and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (>99%; Aldrich). For example, KFeCuZn/ZrO<sub>2</sub> (3, 15, 10, and 5% wt of K, Fe, Zn, and Cu, respectively) was prepared by adding a certain amount of K, Fe, Cu, and Zn precursors and ZrO<sub>2</sub> to a glass vessel (100 mL) containing 20 mL of deionized water. The mixture was stirred at 200 rpm for 60 min at room temperature. Subsequently, water was removed from the mixture by evaporation *in vacuo*, followed by drying at 120 °C under ambient pressure, for ~12 h. The resulting material was calcined for 3 h at 500 °C in air.

### Characterization

X-ray diffraction (XRD) analysis was conducted on a Miniflex (Rigaku) diffractometer using Cu K $\alpha$  radiation. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) were performed using an FEI Titan G2 microscope. The samples were prepared by dropping an ethanolic solution containing a catalyst onto carbon-supported Mo grids. N<sub>2</sub> adsorption measurements were conducted using an AUTOSORB 6AG (Yuasa Ionics) instrument at 77 K. Before the measurements, the calcined pieces of samples were ground and outgassed under vacuum at 200 °C for 3 h. The specific surface areas and pore size distribution of our samples were acquired by the Brunauer–Emmett–Teller (BET) N<sub>2</sub> adsorption measurements.

H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) was performed on a BELCat II instrument with a TCD detector. Briefly, ~100 mg of the catalyst was placed into a quartz tube and purged with Ar at 200 °C (2 h) to remove physically adsorbed water and surface carbonates. Then, the sample was cooled to 50 °C, followed by subsequent heating to 800 °C in 10 vol% H<sub>2</sub> balanced with Ar, at a ramping rate of 10 °C min<sup>-1</sup>.

CO<sub>2</sub> temperature programmed surface reaction (CO<sub>2</sub>-TPSR) was conducted on a BELCat II instrument with a mass spectrometer (BELMass; MicrotracBEL Corp). ~100 mg of catalyst was placed in a quartz tube and reduced by 10% H<sub>2</sub>/Ar at 400 °C for 0.5 hours. The carrier gas was then changed to He and the sample cooled to 50 °C. Subsequently, 10% CO<sub>2</sub>/He was introduced to allow CO<sub>2</sub> adsorption on the catalyst surface for 1 hour. The sample was then heated to 700 °C in a mixture of 10% H<sub>2</sub>/Ar at a ramp rate of 10 °C min<sup>-1</sup>. Ion fragmentation was monitored by BELMass at *m/z* = 40 for Ar, *m/z* = 15 for CH<sub>4</sub>, *m/z* = 28 for CO and *m/z* = 44 for CO<sub>2</sub>.

Pulse hydrogenation measurements were performed in a fixed-bed reactor. In detail, 100 mg of the used KFeCuZn/ZrO<sub>2</sub> catalyst was reactivated under the reaction gas (40 mL min<sup>-1</sup>) at 320 °C for 1 h. After that, a pulse of CH<sub>3</sub>CHO (500  $\mu$ L for every injection) was introduced every 10 min for four cycles under a carrier gas (H<sub>2</sub>/CO<sub>2</sub>/Ar in a ratio of 74.4/24.8/0.8 and the total flow rate is 40 mL min<sup>-1</sup>). The signals of CH<sub>3</sub>CHO and CH<sub>3</sub>-CH<sub>2</sub>OH were monitored using an online mass spectrometer.

*In situ/operando* diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded on a JASCO FT/IR-4600 instrument equipped with a mercury–cadmium–telluride (MCT) detector. The sample was pressed into a DRIFT cell (DR-650 Ci) using a CaF<sub>2</sub> window. The spectra were measured by accumulating 20 scans at a resolution of 8 cm<sup>-1</sup>, 0.5 MPa and temperature range of 200–320 °C. The reference spectrum in He flow (20 scans), taken at the measurement temperature, was subtracted from each spectrum. A high-sampling-rate GC-TCD (490 Micro GC; Agilent Technologies Inc.) was installed at the outlet for the analysis of methanol and ethanol.

Fe K-edge, Cu K-edge, and Zn K-edge X-ray absorption spectroscopy (XAS) were performed in transmission mode at BL01B1 of SPring-8 at the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No.: 2023A1931). A Si (111) double crystal monochromator was used. Boron nitride (BN) was used to make a pellet sample when the required amount was less than 20 mg. The spectra of reference compounds were recorded at room temperature, in air. The obtained XAS spectra were analyzed using the Athena and Artemis software ver. 0.9.26, included in the Demeter package.<sup>41</sup>

For *in situ* XAS measurements, samples in pellet forms ( $\phi$ : 7 mm) were introduced into a cell equipped with Kapton film windows and gas lines connected to the micro-gas chromatograph. Pretreatment of the samples involved heating under a flow of H<sub>2</sub> (300 mL min<sup>-1</sup>) at 300 °C for 30 min. Subsequently, 25% CO<sub>2</sub>/He (400 mL min<sup>-1</sup>), 75% H<sub>2</sub>/He (400 mL min<sup>-1</sup>), and CO<sub>2</sub> (100 mL min<sup>-1</sup>) + H<sub>2</sub> (300 mL min<sup>-1</sup>) were introduced into the cell with He purge intervals between gas introductions.

### Catalytic reaction

CO<sub>2</sub> hydrogenation reactions were conducted in a fixed-bed continuous-flow reactor operating at a total pressure of 4 MPa (40 bar). We used 1% Ar/99% H<sub>2</sub> (purity; H<sub>2</sub>: 99.99999%, Ar: 99.99999%) and CO<sub>2</sub> (purity; 99.995%) gas cylinders to supply the reaction gases. The reactor was supplied with a gas mixture of H<sub>2</sub>/CO<sub>2</sub>/Ar in a ratio of 74.4/24.8/0.8, with Ar serving as an internal standard gas. Prior to the catalytic measurements, 200 mg of the catalyst was placed between quartz wool inside a 1/4 inch fixed-bed reactor (inside diameter: 3.79 mm). The catalyst was pretreated under ambient pressure at a H<sub>2</sub>/Ar (99%) flow rate of 20 mL min<sup>-1</sup> and temperature of 400 °C for 0.5 h. Following the pretreatment, a H<sub>2</sub>/CO<sub>2</sub>/Ar (74.4/24.8/0.8) flow at a total flow rate of 40 mL min<sup>-1</sup> was passed through the catalyst bed at 4 MPa. The weight hourly space velocity (WHSV) was 12 L g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. We conducted an aging treatment for 10 h at 400 °C under the reaction gas atmosphere as an accelerated aging test before recording the results of the catalytic reaction (Fig. S1†).



The products were analyzed using an online gas chromatograph (Shimadzu GC-2014) equipped with TCD (Shincarbon-ST column) and FID (Porapak Q column) detectors, within a reaction temperature range of 240–400 °C.

The CO<sub>2</sub> conversion ( $X_{\text{CO}_2}$ ) was calculated as follows.

$$X_{\text{CO}_2} = \frac{\frac{c_{\text{CO}_2}^{\text{in}}}{c_{\text{Ar}}^{\text{in}}} - \frac{c_{\text{CO}_2}^{\text{out}}}{c_{\text{Ar}}^{\text{out}}}}{\frac{c_{\text{CO}_2}^{\text{in}}}{c_{\text{Ar}}^{\text{in}}}} \times 100\%$$

The selectivity ( $S_i$ ) for individual products was calculated by the following equation:

$$S_i = \frac{c_i \times n_i}{\sum (c_i \times n_i)} \times 100\%$$

Here,  $c_i$  is the molar fraction of product  $i$  (CO, hydrocarbons, or oxygenates), and  $n_i$  is the carbon number of product  $i$  in the reaction.

The EtOH decomposition experiments were conducted in a batch reactor using the spent catalyst. The spent catalyst (50 mg) was placed in a quartz tube and reduced using H<sub>2</sub> at 300 °C for 30 min. Subsequently, ethanol (0.3 mL) and octane (0.7 mL) were introduced into the quartz tube and fixed in a batch reactor. The above mixture was magnetically stirred at 260 °C under N<sub>2</sub> (0.5 MPa) for 3 h. Gas-phase products were collected and analyzed using a GC-FID (Shimadzu GC-2014; Porapak Q column) with a methanizer (Shimadzu MTN-1), whereas the liquid-phase products were analyzed using a gas chromatograph with a GC-FID (Shimadzu GC-14B; Ultra ALLOY capillary column UA<sup>+</sup>-1; Frontier Laboratories, Ltd).

CO hydrogenation and additional CO<sub>2</sub> hydrogenation over the KFeCuZn/ZrO<sub>2</sub> catalyst reactions were conducted in the same fixed-bed continuous-flow reactor with the same WHSV (18.45 L g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>) and operated at the same pressure of 3 MPa for comparison. The reactor was supplied with a gas mixture of H<sub>2</sub>/CO (CO<sub>2</sub>)/Ar in a ratio of 74.4/24.8/0.8 (CO or CO<sub>2</sub>: H<sub>2</sub> = 1:3), with Ar serving as an internal standard gas. We conducted an aging treatment for 10 h at 400 °C under the reaction gas atmosphere as an accelerated aging test before recording the results of the catalytic reaction (as described in Fig. S1†). The products were analyzed using an online gas chromatograph (Shimadzu GC-2014) equipped with TCD (Shincarbon-ST column) and FID (Porapak Q column) detectors, within a reaction temperature range of 240–400 °C.

## Results and discussion

### Catalytic CO<sub>2</sub> hydrogenation to EtOH

CO<sub>2</sub> hydrogenation reactions were conducted under specific operating conditions of  $P = 4$  MPa,  $T = 280$ – $400$  °C, and WHSV = 12 L g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. As shown in Fig. 1a, the KFeCuZn/ZrO<sub>2</sub> catalyst exhibits the highest selectivity towards C<sub>2+</sub> alcohol products, with ~40 and 16.5% selectivity towards C<sub>2+</sub> alcohols and EtOH, respectively, while achieving a CO<sub>2</sub> conversion of 52.4%. In particular, the KFeCuZn/ZrO<sub>2</sub> catalyst also displays an excellent space time yield (STY) of EtOH, with a STY<sub>EtOH</sub> of

5.4 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. In comparison, the CO<sub>2</sub> conversion fell within a comparable range of 49.6–56.7% for the other studied catalysts (KFe/ZrO<sub>2</sub>, KFeCu/ZrO<sub>2</sub> and KFeZn/ZrO<sub>2</sub>). Additionally, for the Cu-added catalyst (KFeCu/ZrO<sub>2</sub>), the EtOH selectivity was approximately 14%, accompanied by a high ethanol space-time yield (STY<sub>EtOH</sub>) reaching up to 4.0 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, which surpasses those of catalysts without Cu (KFe/ZrO<sub>2</sub> and KFeZn/ZrO<sub>2</sub>). This suggests that Cu plays a significant role in facilitating the activation and coupling of CO<sub>2</sub> molecules for ethanol production.<sup>40</sup> Although the addition of Zn (KFeZn/ZrO<sub>2</sub>) did not directly result in an obvious enhancement in EtOH production, the catalyst incorporating both Cu and Zn (KFeCuZn/ZrO<sub>2</sub>) demonstrated the highest selectivity and STY<sub>EtOH</sub>. Literature data on EtOH synthesis from CO<sub>2</sub>/H<sub>2</sub> (Table S1†) are compared with our best catalytic system. Our catalyst displayed the best STY<sub>EtOH</sub> for EtOH synthesis even after the accelerated aging test at 400 °C for 10 h.

To emphasize the pivotal roles of potassium and iron, we intentionally omitted these elements from the compared catalysts, as illustrated in Fig. 1a. Notably, the FeCuZn/ZrO<sub>2</sub> catalyst, while maintaining a CO<sub>2</sub> conversion of 47% comparable to that of the KFeZnCu/ZrO<sub>2</sub> catalyst, exhibited a significant increase in CH<sub>4</sub> selectivity, reaching 37%. Simultaneously, the selectivity for total alcohols and EtOH decreased sharply to 9 and 3.4%, respectively. Furthermore, the STY<sub>EtOH</sub> for the FeCuZn/ZrO<sub>2</sub> catalyst was measured at 0.6 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. This significantly reduced alcohol activity in the absence of K underscores the essential role of K in C<sub>2+</sub> alcohol synthesis and the inhibition of over-hydrogenation.<sup>34,39,40</sup> The EtOH production significantly decreased over the KCuZn/ZrO<sub>2</sub> catalyst under the same

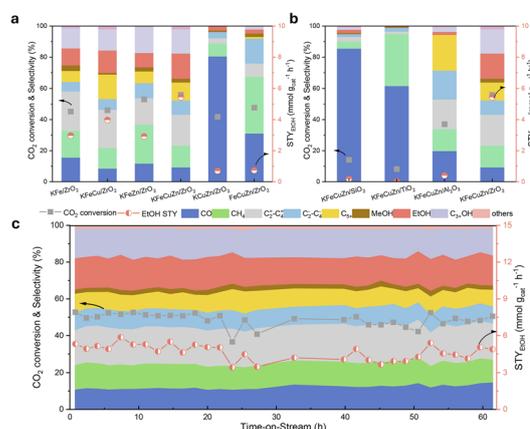


Fig. 1 Catalytic performance. (a) CO<sub>2</sub> conversion and product selectivity at 360 °C and STY<sub>EtOH</sub> over KFe/ZrO<sub>2</sub> based catalysts; (b) CO<sub>2</sub> conversion, product selectivity, and STY<sub>EtOH</sub> over different supporting; and (c) stability test for KFeCuZn/ZrO<sub>2</sub> at 360 °C. Pretreatment condition: 400 °C, 0.1 MPa, H<sub>2</sub> (99%), and 0.5 h. Reaction condition: 12 L g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, 4.0 MPa, and H<sub>2</sub>/CO<sub>2</sub>/Ar (74.4/24.8/0.8%). Ar was used as an internal standard gas. The data was collected after 3 h, when the temperature and reaction were stable. Accelerated aging treatment was performed before reaction at 400 °C for 10 h under the reaction environment. Others include acetaldehyde and ethyl formate. In (a) and (b), the gray dot is CO<sub>2</sub> conversion; red dot is EtOH STY.



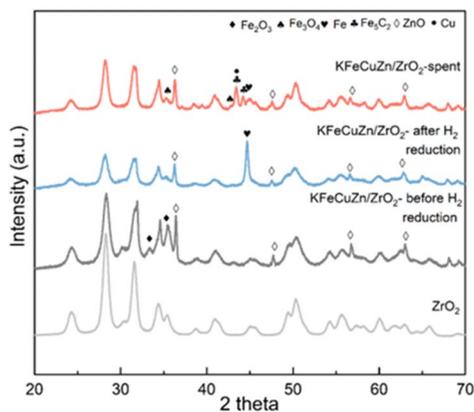


Fig. 2 XRD patterns of KFeCuZn/ZrO<sub>2</sub> before and after H<sub>2</sub> reduction at 400 °C as a pretreatment and after reaction. "Spent catalyst" refers to a sample that has undergone a 20 hours accelerated aging treatment at 400 °C under the reaction conditions.

conditions because of the absence of Fe, which resulted in the loss of the ability of the catalyst for C–C coupling.<sup>42,43</sup> Furthermore, Fig. S2† displayed a volcano-shaped curve for STY<sub>EtOH</sub> with increasing Fe loading, and the most suitable loading is 15%<sub>wr</sub>. Fig. 1b illustrates CO<sub>2</sub> hydrogenation experiments using different supports, such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and SiO<sub>2</sub>. All three catalysts showed an obvious decrease in the EtOH selectivity to less than 2%. In terms of STY<sub>EtOH</sub>, the KFeZnCu/ZrO<sub>2</sub> catalyst significantly outperformed the others, indicating that ZrO<sub>2</sub> is an excellent carrier for EtOH synthesis.

In addition, the effects of the reaction conditions, including reaction temperature, pressure, and WHSV, on EtOH synthesis were investigated in detail. On varying the reaction temperature within the range of 280–400 °C (Fig. S3†), the STY of EtOH and C<sub>2+</sub> alcohol distribution exhibited a characteristic volcano-shaped curve. The appropriate temperature for acquiring EtOH is 360 °C. Additionally, the reaction pressure was varied from 3 to 5 MPa (Fig. S4a†), and the highest STY<sub>EtOH</sub> (5.4 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>) were achieved at 4 MPa, making it a more favorable pressure regime for C<sub>2+</sub> alcohol synthesis. Furthermore, we explored the influence of the WHSV (Fig. S4b†) by varying it between 9–15 L g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> and observed the most suitable WHSV was 12 L g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. Moreover, the stability test was performed for the KFe-based catalysts (Fig. 1c and S5†). Among them, KFeCu/ZrO<sub>2</sub>, KFeZn/ZrO<sub>2</sub> and KFeCuZn/ZrO<sub>2</sub> showed robust stability, maintaining their performance for at least 60 h at 360 °C. Only KFe/ZrO<sub>2</sub> displayed slight decrease in STY<sub>EtOH</sub> after 35 h. Additionally, a simplified version of Fig. 1 was provided as Fig. S6† by replacing the selectivity of C<sub>2</sub><sup>-</sup>–C<sub>4</sub><sup>-</sup>, C<sub>2</sub><sup>-</sup>–C<sub>4</sub><sup>-</sup>, and C<sub>5+</sub> to C<sub>2+</sub> hydrocarbons.

### Structural characterization

Multiple characterization methods were used to reveal the physical characterizations and structural evolution. The BET specific surface areas and pore volumes (Table S2†), obtained from the N<sub>2</sub> adsorption measurements at 77 K, decreased upon increase in loading amount of the supported species. Pore size

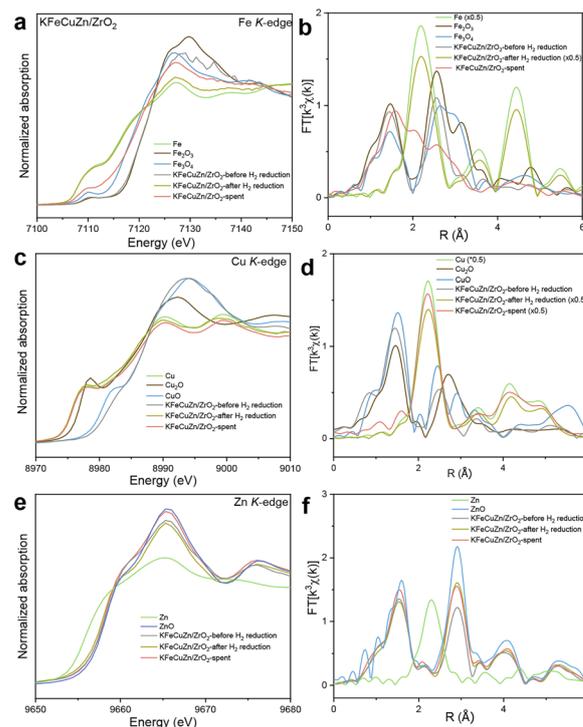


Fig. 3 *Ex situ* XAS spectra of KFeCuZn/ZrO<sub>2</sub> before and after H<sub>2</sub> reduction at 400 °C as a pretreatment and after reaction (spent). (a) Normalized Fe K-edge XANES spectra; (b) FT-EXAFS spectra for Fe; (c) normalized Cu K-edge XANES spectra; (d) FT-EXAFS spectra for Cu; (e) normalized Zn K-edge XANES spectra; and (f) FT-EXAFS spectra for Zn. "Spent catalyst" refers to a sample that has undergone a 20 hours accelerated aging treatment at 400 °C under the reaction condition.

distributions were not significantly different among samples measured (Fig. S7†). XRD patterns (Fig. 2) show that the ZrO<sub>2</sub> support is composed of monoclinic and minor tetragonal phases based on the diffraction angles and intensities. Phase transformations of the loading elements were also observed at different reaction stages. For example, for the KFeCuZn/ZrO<sub>2</sub> catalyst, metallic Fe was obtained after H<sub>2</sub> reduction pretreatment (Fig. 2); subsequently, metallic Fe was oxidized to Fe<sub>3</sub>O<sub>4</sub> and carburized to Fe<sub>5</sub>C<sub>2</sub> after the reaction.<sup>42,44</sup> Iron carbide (Fe<sub>5</sub>C<sub>2</sub>) is an essential phase for C–C coupling in the Fischer–Tropsch (F–T) process over Fe-based catalysts.<sup>42</sup> Cu-derived peaks were not observed by XRD after calcination and reduction, probably due to the highly dispersed nature of Cu. Metallic copper was observed after the reaction owing to the sintering of Cu under a reductive atmosphere for a longer time. For the Zn species, only ZnO diffraction peaks were observed, indicating that no phase changes occurred during the entire reaction process. In comparison with the other control catalysts (Fig. S8†), the same evolution processes (reduction and carburization of Fe, reduction and aggregation of Cu, and stability of ZnO on Zn) were observed for the catalysts containing the relative elements.

To further clarify the phase transformations of Fe, Cu, and Zn species, X-ray adsorption spectroscopy (XAS) was performed



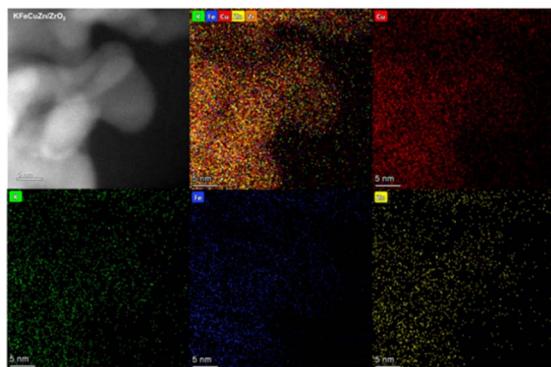


Fig. 4 HAADF-STEM image and corresponding EDS mapping images of the fresh KFeCuZn/ZrO<sub>2</sub> that has undergone calcination at 500 °C under air.

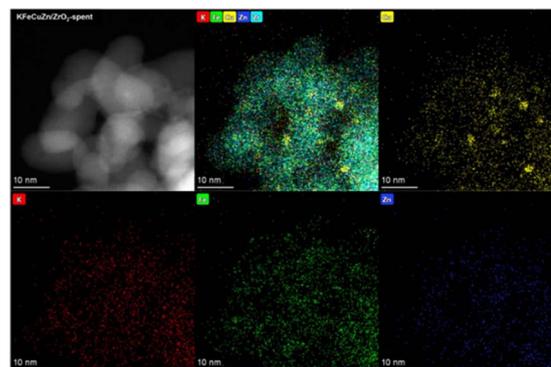


Fig. 5 HAADF-STEM image and corresponding EDS mapping images of the spent KFeCuZn/ZrO<sub>2</sub> that has undergone a 20 hours accelerated aging treatment at 400 °C under the reaction condition.

on KFeCuZn/ZrO<sub>2</sub>. The *ex situ* X-ray absorption near edge structure (XANES) spectra of the Fe K-edge (Fig. 3a) show that after H<sub>2</sub> reduction as the pretreatment, the absorption edge shifted to almost the same energy as that of the Fe foil, suggesting that the Fe species in KFeZnCu/ZrO<sub>2</sub> were completely reduced. Similarly, after the reaction, the absorption edge moved to a higher energy compared to that of the Fe foil, suggesting the partial oxidation of Fe, in line with the XRD results. Extended X-ray absorption fine structure (EXAFS) results further helped to understand the local environmental changes (Fig. 3b and Table S3<sup>†</sup>). After the H<sub>2</sub> reduction pretreatment, the Fe–Fe bonds at 2.45 and 2.83 Å appeared, whereas the Fe–O bond at 1.99 Å disappeared.<sup>45,46</sup> After the reaction, Fe–C and Fe–O appeared, and the Fe–Fe bond weakened, indicating the generation of FeO<sub>x</sub> and FeC<sub>x</sub>, consistent with the XRD results. In the case of Cu (Fig. 3c), as exhibited in *ex situ* XANES spectra, CuO was reduced to metallic Cu after reduction, which was maintained until the end of the reaction, as supported by the curve fitting of the EXAFS spectra (Fig. 3d and Table S4<sup>†</sup>). Additionally, as indicated by the Zn K-edge XANES (Fig. 3e), after reduction, a weak shift to a lower energy was observed, implying the presence of a minor amount of metallic Zn, as confirmed by the EXAFS curve fitting results (Fig. 3f and Table S5<sup>†</sup>). In contrast, after the reaction, the energy increased to that of the closed ZnO reference and only one component of ZnO was captured (Table S5<sup>†</sup>), indicating that the zinc species prefers oxygen over hydrogen.<sup>47</sup>

H<sub>2</sub>-TPR experiments were carried out to clarify the reduction ability of different additive elements and H<sub>2</sub> activation capacity over different catalysts. As depicted in Fig. S9,<sup>†</sup> considering mono-component supported catalysts such as Fe/ZrO<sub>2</sub>, Cu/ZrO<sub>2</sub>, and Zn/ZrO<sub>2</sub>, Cu displayed the lowest reduction temperature and was the most readily reduced element, followed by Fe. In agreement with the XRD and XAS results, no reduction was observed in the ZnO content. In contrast, the introduction of K could promote the generation of reduction peak at 600 °C, unlike with pure ZrO<sub>2</sub>.<sup>40</sup> Contrastingly, after loading the promoter, the reduction temperatures of Fe and Cu increased for KFe/ZrO<sub>2</sub> and KCu/ZrO<sub>2</sub>, inhibiting the reduction of the active elements.<sup>39,40</sup> Furthermore, in comparison with KFe/ZrO<sub>2</sub>

and KFeCu/ZrO<sub>2</sub>, the temperature for the reduction of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> on the KFeCu/ZrO<sub>2</sub> catalyst decreased to 390 °C.<sup>48</sup> In contrast, the reduction temperature of FeO<sub>x</sub> remained virtually unchanged over the KFeZn/ZrO<sub>2</sub> catalyst, suggesting that the introduction of Zn was ineffective in promoting the reduction of the Fe species. However, after loading Zn into KFeCu/ZrO<sub>2</sub>, the reduction temperature increased slightly, indicating that the introduction of Zn led to a decrease in the reduction ability.<sup>47,49</sup>

HAADF-STEM and EDS were performed for fresh and spent KFeCuZn/ZrO<sub>2</sub>, as shown in Fig. 4 and 5, respectively. Because of the weak Z-contrast, identifying the crystal phase and interplanar spacing of the Fe, Cu, and Zn species was challenging. Therefore, we only observed the elemental distributions. The HAADF-STEM and EDS elemental mapping images revealed that K, Fe, Cu, and Zn over the KFeCuZn/ZrO<sub>2</sub> catalyst were homogeneously distributed on ZrO<sub>2</sub> for fresh KFeCuZn/ZrO<sub>2</sub>

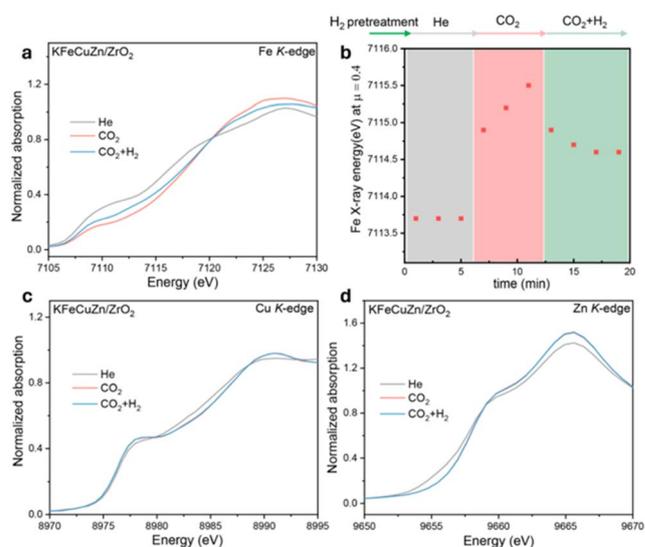


Fig. 6 *In situ* XAFS spectra of KFeCuZn/ZrO<sub>2</sub>. (a) Normalized Fe K-edge XANES spectra; (b) X-ray energy at normalized absorption ( $\mu = 0.4$ ) under different atmospheres; (c) Cu K-edge XANES spectra; and (d) Zn K-edge XANES spectra. Conditions: 400 °C and 1 bar.



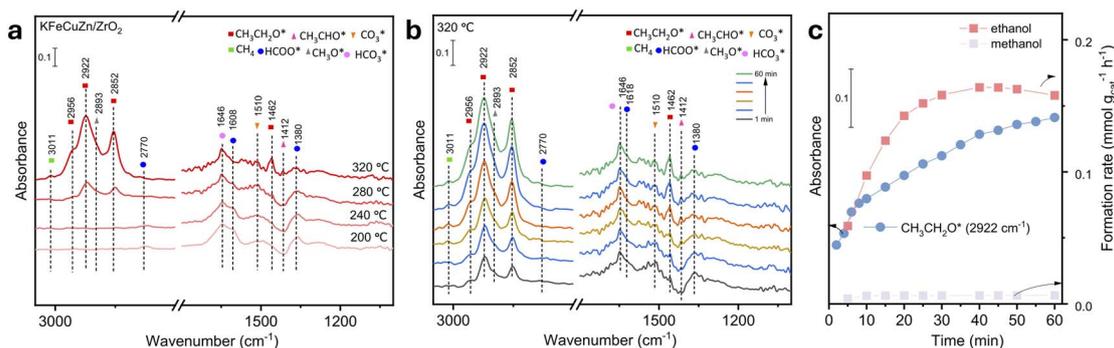


Fig. 7 *In situ/operando* DRIFTS spectra. (a) DRIFTS spectra of the  $\text{CO}_2 + \text{H}_2$  reaction over  $\text{KFeCuZn/ZrO}_2$  after 60 min at 0.5 MPa and different temperatures; (b) time resolution spectra of the  $\text{CO}_2 + \text{H}_2$  reaction over  $\text{KFeCuZn/ZrO}_2$  at 0.5 MPa and 320 °C; (c) dynamic IR peak intensities of  $\text{CH}_3\text{CH}_2\text{O}^*$  ( $2922\text{ cm}^{-1}$ ) and formation rate of ethanol and methanol, quantified by micro-GC at 320 °C.

(Fig. 4). After the reaction, K, Fe, and Zn remained highly dispersed in  $\text{ZrO}_2$  (Fig. S10<sup>†</sup> and 5). The particle size of Cu increased a little, indicating the aggregation of Cu over  $\text{KFeCuZn/ZrO}_2$ . In comparison, larger Cu nanoparticles were observed over the spent  $\text{KFeCu/ZrO}_2$ , elucidating that the introduction of Zn limited Cu sintering (Fig. 5 and S11–S13<sup>†</sup>). Inhibition of sintering of Cu nanoparticles was also reported for Cs–CuZnFe<sup>30</sup> and  $\text{CuZnO–Al}_2\text{O}_3$  (ref. 50) systems.

### Mechanistic studies

*In situ* XAS was employed to clarify the chemical states under  $\text{He}$ ,  $\text{CO}_2$ , and  $\text{CO}_2 + \text{H}_2$  atmospheres at 400 °C and ambient pressure after  $\text{H}_2$  pretreatment. The Fe K-edge XANES spectra (Fig. 6a) of  $\text{KFeCuZn/ZrO}_2$  clearly showed that the absorption edge shifted to higher energies after the introduction of  $\text{CO}_2$  (Fig. 6b), indicating that the Fe species were oxidized by  $\text{CO}_2$ . These results clearly proved that  $\text{CO}_2$  functioned as an oxidizing agent, facilitating the oxidation of Fe species.<sup>51</sup>

For the Cu K-edge and Zn K-edge, although there were minor shifts upon the introduction of  $\text{CO}_2$ , the edge positions remained almost unchanged upon the introduction of  $\text{CO}_2 + \text{H}_2$ . These results suggested that the redox reactions of Cu and Zn were not involved in the  $\text{CO}_2$  hydrogenation reaction.

The *in situ/operando* DRIFTS was performed to elucidate the mechanism underlying the hydrogenation of  $\text{CO}_2$  to EtOH and role of each element. These *in situ/operando* DRIFTS experiments were conducted under specific conditions, including a pressure of 0.5 MPa, temperature of 320 °C (with an exception for  $\text{KFeCuZn/ZrO}_2$ , where the temperature range was 200–320 °C), and  $\text{H}_2 : \text{CO}_2$  ratio of 3 : 1. The critical assignments of the surface species and adsorbed methanol and ethanol species are provided in Table S6 and Fig. S14.<sup>†</sup> Observations at 200 °C for  $\text{KFeCuZn/ZrO}_2$  indicate the presence of adsorbed  $\text{CO}_2$  at 1269 and  $1514\text{ cm}^{-1}$ ,<sup>30,52</sup> which can be attributed to the carbonate species (bicarbonate species at  $1620\text{ cm}^{-1}$ )<sup>53</sup> and surface formate located at  $2775/1593/1393\text{ cm}^{-1}$ .<sup>22,40,54</sup> No  $\text{CH}_3\text{O}^*$  or  $\text{CH}_3\text{CH}_2\text{O}^*$  were detected (Fig. S15a<sup>†</sup> and 7a). After the reaction temperature increased to 240 °C (Fig. S15b<sup>†</sup>), a weak peak, which can be attributed to an important intermediate of  $\text{CH}_3\text{-CHO}^*$  in EtOH synthesis, was observed at  $1410\text{ cm}^{-1}$ .<sup>40</sup> When

the temperature reached 280 °C (Fig. S16a<sup>†</sup>), with an increase in the exposure time, the intensity of the  $\text{CH}_3\text{CHO}^*$  assignment gradually increased at  $1410\text{ cm}^{-1}$ . After  $\sim 25$  min, it was consumed, and subsequently, peaks assignable to ethoxy ( $2852/2922/2956\text{ cm}^{-1}$ ) were observed.<sup>27,30,39</sup> In addition, EtOH in gas phase was tracked and quantified using online gas chromatography (Fig. S16b<sup>†</sup>). A  $\text{CH}_3\text{CHO}$  pulse experiment was also performed in a  $\text{CO}_2 + \text{H}_2$  environment using the spent  $\text{KFeZnCu/ZrO}_2$  catalyst (Fig. S17<sup>†</sup>). The introduction of  $\text{CH}_3\text{CHO}$  into the reaction environment resulted in a rapid increase in the intensity of the  $\text{CH}_3\text{CH}_2\text{OH}$  signal. This clearly indicates that the hydrogenation of  $\text{CH}_3\text{CHO}$  to  $\text{CH}_3\text{CH}_2\text{OH}$  is highly facile under the given conditions. Furthermore, the DRIFTS spectra also showed a minor peak at  $2820\text{ cm}^{-1}$ , which can be assigned to  $\text{CH}_3\text{O}^*$ ,<sup>30,54</sup> along with a decrease in the intensity of the peak at  $2770\text{ cm}^{-1}$ , assignable to formate. Upon reaching a temperature of 320 °C, the intensity of  $\text{CH}_3\text{CH}_2\text{O}^*$  became more pronounced (Fig. 7b). In addition, another assignment appeared, with  $\text{CH}_3\text{CH}_2\text{O}^*$  characterized by  $\delta(\text{CH}_2)$  vibrations at  $1462\text{ cm}^{-1}$ .<sup>40</sup> The methane appeared at  $3011\text{ cm}^{-1}$ ,<sup>39,40</sup> which was not seen at lower temperatures. Notably, some papers reported that the peaks for  $\text{CH}_3\text{CH}_2\text{O}^*$  and  $\text{CH}_3\text{O}^*$  overlapped in the  $2940\text{--}2980\text{ cm}^{-1}$  region.<sup>27,30</sup> According to the quantification of the micro-GC results the formation rate of EtOH was much higher than that of methanol (Fig. 7c). Thus, we assigned the peaks at 2852, 2922, and

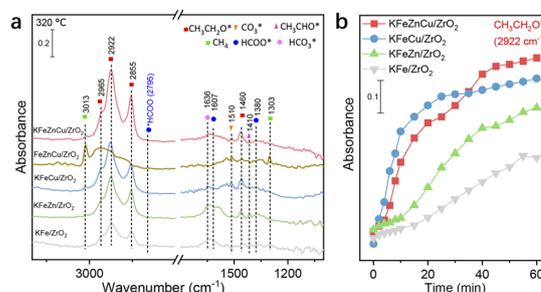


Fig. 8 *In situ* DRIFTS spectra. (a) Different catalysts under the  $\text{CO}_2 + \text{H}_2$  reaction after 60 min at 320 °C and 0.5 MPa; (b) dynamic IR peak intensities of  $\text{CH}_3\text{CH}_2\text{O}^*$  ( $2922\text{ cm}^{-1}$ ) at 320 °C for different catalysts.



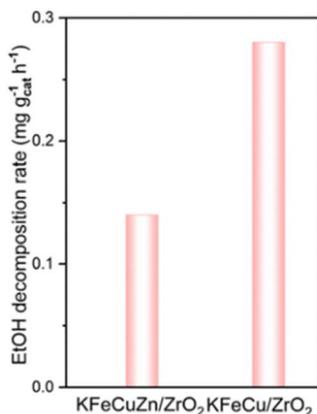


Fig. 9 EtOH decomposition over the KFeCuZn/ZrO<sub>2</sub> and KFeCu/ZrO<sub>2</sub> catalysts (conditions: batch reactor, spent catalysts: 50 mg, N<sub>2</sub>: 0.5 MPa, at 260 °C, 3 h, ethanol (0.3 mL) + octane (0.7 mL)).

2956 cm<sup>-1</sup> to CH<sub>3</sub>CH<sub>2</sub>O\*, which is regarded as an important intermediate for EtOH formation.<sup>27,30</sup>

DRIFTS experiments were also conducted on various catalysts to identify the roles of the different elements. KFeCuZn/ZrO<sub>2</sub> catalyst displayed the highest CH<sub>3</sub>CH<sub>2</sub>O\* intensity after 60 min (Fig. 8a). In comparison, the FeCuZn/ZrO<sub>2</sub> catalyst exhibited strong CH<sub>4</sub> peaks at 1302 and 3011 cm<sup>-1</sup> during DRIFTS analysis (Fig. 8a and S18†),<sup>55</sup> which indicated K enabled suppression of CH<sub>4</sub> formation.<sup>40,56</sup> Simultaneously, there was a significant decrease in produced EtOH, the amount of adsorbed carbonate<sup>30,52</sup> at 1268 and 1510 cm<sup>-1</sup> and formate species<sup>22,40,54</sup> at 1388 and 1594 cm<sup>-1</sup>. These results indicate that the addition of potassium has a positive impact on enhancing CO<sub>2</sub> adsorption/activation and facilitates alcohol synthesis. In contrast, KFe/ZrO<sub>2</sub>, KFeZn/ZrO<sub>2</sub>, and KFeCu/ZrO<sub>2</sub> showed similar surface species but with variations in intensity compared to the KFeCuZn/ZrO<sub>2</sub> catalyst, indicating the same mechanism with different efficiencies (Fig. 8a and S19†). The evolution of CH<sub>3</sub>CH<sub>2</sub>O\* is shown in Fig. 8b. The peak intensities of CH<sub>3</sub>CH<sub>2</sub>O\* over KFeCuZn/ZrO<sub>2</sub> and KFeCu/ZrO<sub>2</sub> are similar and higher than those of the catalysts without Cu. This indicates that the addition of Cu is helpful for the evolution of

CH<sub>3</sub>CH<sub>2</sub>O\*, leading to EtOH formation. Concretely, introduction of Cu significantly promotes the formation of CO (CO<sub>2</sub>-TPSR, Fig. S20†). It was reported<sup>30,39,40,46</sup> that increased CO provides a great chance of coupling with CH<sub>x</sub> on iron carbide surface to form CH<sub>3</sub>CHO, which in turn is hydrogenated to CH<sub>3</sub>CH<sub>2</sub>O\* and subsequently CH<sub>3</sub>CH<sub>2</sub>OH, over Fe–Cu based catalysts. Because of the similar catalyst components, it is thought that EtOH was produced *via* the same pathway over our catalyst. Simultaneously, as previously reported, Cu helps non-dissociative activation of CO and its coupling with alkyl (CH<sub>x</sub>) species to form ethanol.<sup>30,39,40,46</sup> Therefore, for KFe/ZrO<sub>2</sub> and KFeZn/ZrO<sub>2</sub> catalysts, the lack of Cu would result in the slight increase of CO and CH<sub>4</sub> selectivity. Although the Zn-assisted KFeCu/ZrO<sub>2</sub> catalyst showed a higher selectivity for EtOH and STY<sub>EtOH</sub>, the difference between KFeCuZn/ZrO<sub>2</sub> and KFeCu/ZrO<sub>2</sub> remains unclear, according to DRIFT results (Fig. 1a).

CO<sub>2</sub> adsorption and EtOH decomposition experiments were conducted to elucidate the role and impact of Zn in EtOH synthesis. The DRIFTS results for CO<sub>2</sub> adsorption (Fig. S21†) revealed that the addition of Zn to the KFeZn/ZrO<sub>2</sub> and KFeCuZn/ZrO<sub>2</sub> catalysts enhanced CO<sub>2</sub> adsorption, leading to more formate and carbonates. The results of the ethanol decomposition experiments over KFeCu/ZrO<sub>2</sub> and KFeCuZn/ZrO<sub>2</sub> using a batch reactor are shown in Fig. 9. The carbonaceous products by the ethanol decomposition are CO<sub>x</sub>, CH<sub>4</sub> and acetaldehyde over KFeCuZn/ZrO<sub>2</sub> and KFeCu/ZrO<sub>2</sub> catalysts, with the CH<sub>3</sub>-CH<sub>2</sub>OH decomposition rate of 0.13 and 0.28 mg g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, respectively. This result indicates that the presence of Zn restricts EtOH decomposition (backward reaction), leading to higher selectivity toward EtOH.

### CO hydrogenation over KFeCuZn/ZrO<sub>2</sub>

Although the one-step conversion of CO<sub>2</sub> to value-added chemicals such as EtOH is attractive, the kinetically unreactive and thermodynamically stable nature of CO<sub>2</sub> pose significant challenges.<sup>8,28,57,58</sup> CO hydrogenation to EtOH is another promising method for producing EtOH;<sup>59–63</sup> thus, we briefly explored the application of our catalysts in CO hydrogenation.<sup>64–69</sup> CO<sub>2</sub> and CO hydrogenation experiments were conducted on the KFeCuZn/ZrO<sub>2</sub> catalyst under the same

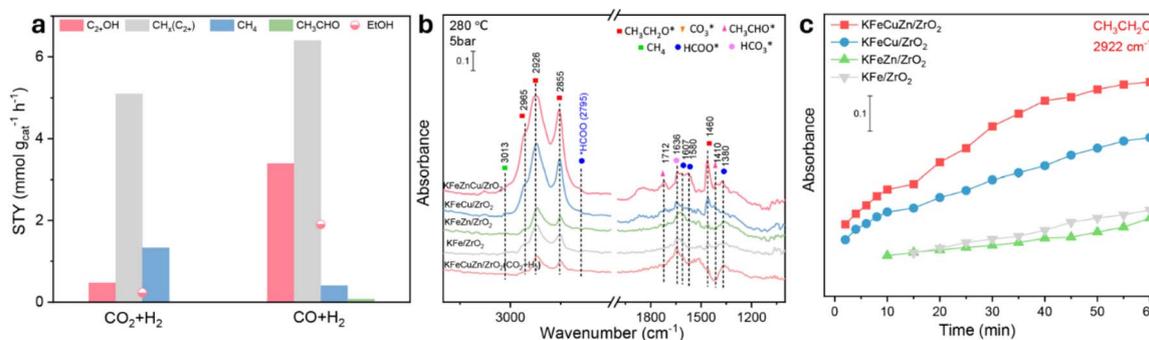


Fig. 10 (a) Catalytic performance over the KFeCuZn/ZrO<sub>2</sub> catalyst under a CO<sub>2</sub>/H<sub>2</sub> or CO/H<sub>2</sub> flow at 280 °C and 3 MPa; (b) *in situ* DRIFTS spectra of the CO + H<sub>2</sub> reaction over the different catalysts under a CO/H<sub>2</sub> flow at 280 °C and 0.5 MPa; and (c) dynamic IR peak intensities of CH<sub>3</sub>CH<sub>2</sub>O\* (2922 cm<sup>-1</sup>) at 280 °C.



experimental conditions of 280 °C, 3 MPa, and CO or CO<sub>2</sub> : H<sub>2</sub> = 1 : 3. The performance results revealed a higher STY of EtOH (1.8 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>) in CO hydrogenation (Fig. 10a). Furthermore, in a comparison of the CO<sub>2</sub> + H<sub>2</sub> DRIFTS experiments, a higher amount of CH<sub>3</sub>CH<sub>2</sub>O\* (2852, 2922, 2956 cm<sup>-1</sup>)<sup>27,30</sup> was observed in the CO<sub>2</sub> (20% CO) + H<sub>2</sub> DRIFTS experiments on KFeCuZn/ZrO<sub>2</sub> (Fig. S22†). These two experiments imply that CO hydrogenation to EtOH is more facile than CO<sub>2</sub> hydrogenation. In addition, CO + H<sub>2</sub> *in situ* DRIFTS was performed to clarify the potential roles of each element. According to the acquired IR spectra (Fig. 10b), the intermediates were similar to those observed in the CO<sub>2</sub> + H<sub>2</sub> DRIFTS results. The intensity of the peak at 1712 cm<sup>-1</sup>, attributed to CH<sub>3</sub>CHO\* over KFeCuZn/ZrO<sub>2</sub>, was found to be higher compared to the other catalysts.<sup>30,70</sup> Additionally, KFeCuZn/ZrO<sub>2</sub> displayed stronger peaks at 2852, 2922, and 2956 cm<sup>-1</sup>, corresponding to CH<sub>3</sub>CH<sub>2</sub>O\* (Fig. 10b, c and S23†), in comparison to the other catalysts.<sup>27,30,39,40</sup> The CH<sub>3</sub>CH<sub>2</sub>O\* intensities of KFe/ZrO<sub>2</sub> and KFeZn/ZrO<sub>2</sub> were similar and much weaker than those of KFeCuZn/ZrO<sub>2</sub> (Fig. 10c).

## Conclusion

In summary, we reported an efficient catalyst for ethanol synthesis, namely KFeCuZn/ZrO<sub>2</sub>, which achieves the STY<sub>EtOH</sub> of 5.4 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> under the optimized conditions (360 °C, 4 MPa, and 12 L g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>) and elucidated the essential roles of K, Fe, Cu, and Zn in EtOH synthesis. *In situ/operando* spectroscopic techniques and various characterizations revealed the essential roles of K and Fe in EtOH synthesis. The introduction of Cu accelerated the generation of CH<sub>3</sub>CH<sub>2</sub>O\*, which is an important intermediate in EtOH production. The addition of Zn inhibited EtOH decomposition, thereby improving the efficiency of EtOH synthesis. The importance of all the components was proven and emphasized in CO<sub>2</sub> hydrogenation to EtOH. Finally, this catalyst demonstrated high performance in EtOH synthesis from syngas (CO + H<sub>2</sub>).

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

Takashi Toyao and Ken-ichi Shimizu supervised this research. Pengfei Du and Abdellah Ait El Fakir co-conducted the experiments and co-wrote the manuscript. Shirun Zhao, Yucheng Qian and HongLi Pan helped to perform the experiments and analyze the data. Nazmul Hasan MD Dostagir, Kah Wei Ting, and Shinya Mine discussed the data and commented on the manuscript.

## Conflicts of interest

There are no conflicts of interest to declare.

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