Previously, we reported a strong Fe-Cu synergy in CO2 hydrogenation to olefin-rich C2+ hydrocarbons over the $\gamma$-Al2O3 supported bimetallic Fe-Cu catalysts. In this work, we aimed to clarify such a synergy by investigating the catalyst structure, Fe-Cu interaction, and catalyst surface properties through a series of characterizations. H2-TPR results showed that the addition of Cu made both Fe and Cu easier to reduce via the strong interaction between Fe and Cu. It was further confirmed by X-ray absorption spectroscopy (XAS) and TEM, which showed the presence of metallic Fe and Fe-Cu alloy phases in the reduced Fe-Cu(0.17) catalyst induced by Cu addition. By correlating TPD results with the reaction performance, we found that the addition of Cu enhanced both the moderately and strongly adsorbed H2 and CO2 species, consequently enhanced CO2 conversion and C2+ selectivity. Adding K increased the adsorbed-CO2/adsorbed-H2 ratio by greatly enhancing the moderately and strongly adsorbed CO2 and slightly suppressing the moderately and strongly adsorbed H2, resulting in a significantly increased O/P ratio in the produced hydrocarbons. The product distribution analysis and in situ DRIFTS suggested that CO2 hydrogenation over the Fe-Cu catalyst involved both an indirect route with CO as the primary product and a direct route to higher hydrocarbons.

**Keywords:** CO2 hydrogenation, characterization, Fe-Cu catalyst, K promotion, CO2 adsorption, H2 adsorption

**INTRODUCTION**

Waste CO2 can be utilized as a carbon source to synthesize valuable chemicals and transportation fuels. Recently, using renewable energy to conduct catalytic CO2 conversion is attracting increased attention, as it has the potential on mitigating both CO2 emissions and the fossil fuel dependence (Song, 2006; Wang et al., 2011; Hu et al., 2013a; Meylan et al., 2015). CO2 is a highly thermodynamically stable molecule ($\Delta G^\circ = -394$ kJ/mol). Thus, a high energy input is normally required for CO2 conversion, especially when CO2 is the solo reactant. However, such an energy
understand the mechanistic roles of these promoters. However, more studies are still needed to well catalysts (Hu et al., 2019; Prašnikar et al., 2011; Prašnikar et al., 2021) [such as methanol over Cu-based catalysts (Huš et al., 2017; Prašnikar et al., 2019; Prašnikar et al., 2021)] and hydrocarbons (Willauer et al., 2013; Satthawong et al., 2015; Zhang et al., 2015) from CO2 and H2, where CO2 is captured from flue gas and H2 is produced using renewable energy sources (e.g., such as solar or wind) (Pontzen et al., 2011), is one promising approach for sustainable production of chemicals and fuels. Among them, C2-C4 light olefins are primary building blocks for various chemicals and polymers. Therefore, developing effective catalysts for selective conversion of CO2 to light olefins is highly desired (Riedel et al., 1999; Song, 2002; Song, 2006; Centi and Perathoner, 2009; Wang et al., 2011).

Fe catalysts have shown activities for both the reverse water-gas shift (RWGS) reaction and Fisher–Tropsch synthesis (FTS) reaction, hence have also been studied for CO2 hydrogenation to synthesize hydrocarbons. However, monometallic Fe catalysts often exhibit low CO2 conversion and primarily produce methane (Wang et al., 2018). To improve CO2 conversion and C2+ selectivity, different promoters have been evaluated (Nam et al., 1997; Yan et al., 2000; Riedel et al., 2001; Ngantsoue-Hoc et al., 2002; Lögdberg et al., 2009; Dorner et al., 2011; Satthawong et al., 2013a; Hu et al., 2013b; Satthawong et al., 2013b; Rodemerck et al., 2013; Fischer et al., 2015; Amoyal et al., 2017; Liu et al., 2018; Wei et al., 2018). For example, the use of CeO2 increases both CO2 conversion and olefin formation (Dorner et al., 2011). Adding V, Cr, Mn, and Zn can also increase CO2 conversion by promoting generation of the iron carbide phase (Nam et al., 1997). Furthermore, the addition of alkali metals enhances catalytic activity as those substances can increase CO2 uptake and facilitate Fe carburization (Riedel et al., 2001; Ngantsoue-Hoc et al., 2002; Fischer et al., 2015; Visconti et al., 2017). However, more studies are still needed to well understand the mechanistic roles of these promoters.

Whether hydrocarbons from CO2 hydrogenation are through a direct or indirect mechanism is under debate. Many believe in the indirect mechanism because CO2 hydrogenation is considered as a modified version of FTS, where CO2 is converted to hydrocarbons through a process involving two steps: CO2 is first reduced to CO (which is the so-called RWGS reaction) and the formed CO is then converted to hydrocarbons through FTS (Lee et al., 2009; Saiedi et al., 2014). It is also suggested by some literature that CO2 is directly hydrogenated to methane, which contributes to the majority of hydrocarbons formation (Fujita et al., 1987; Schild et al., 1991; Wei and Jinlong, 2010).

In our previous work, we discovered a strong bimetallic Fe-Cu synergy in CO2 conversion and C2+ hydrocarbons formation when Cu was added to Fe at a certain composition. Adding Cu to Fe enhanced the formation of CO and C2+ hydrocarbons and suppressed CH4 formation. The production of C2-C4 olefin-rich hydrocarbons was promoted dramatically when K was incorporated into the Fe-Cu bimetallic catalysts, in which, the C2-C4 olefin to paraffin ratio reached as much as 5.2 (Wang et al., 2018). The DFT simulation suggested that the addition of Cu dramatically shifted the reaction pathway. On mono-metallic Cu and Fe catalysts, the main pathway included the formation of CO and subsequent CO hydrogenation to CH* species (Riedel et al., 2001; Satthawong et al., 2015). In contrast, over the Fe-Cu bimetallic catalysts, a new and completely different reaction pathway was favored, which did not go through CO as the intermediate (Nie et al., 2016; Nie et al., 2017). As a result, more C2+ hydrocarbons were produced, exhibiting a strong Fe-Cu synergetic effect.

To better understand such Fe-Cu synergetic effects observed in our previous work, in this study, we performed a detailed catalyst characterization and investigated the relationship between the physical structure and catalytic performance of Fe-Cu catalysts in CO2 hydrogenation to C2+ hydrocarbons. A series of fresh, reduced, and spent Fe-Cu catalysts with different Cu/Fe atomic ratios were investigated by various characterization techniques including H2 temperature-programmed reduction (H2-TPR), transmission electron microscopy (TEM), scanning transmission electron microscopy/energy dispersive X-ray spectroscopy (STEM/EDS), Fe K-edge X-ray absorption spectroscopy (XAS), in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and temperature-programmed desorption of hydrogen and carbon dioxide (H2-TPD and CO2-TPD). In combination with the catalytic reaction data, we systematically examined the mechanistic roles of Fe-Cu bimetallic composition and K promoter, and their influences on CO2 conversion and the formation of olefin-rich C2+ hydrocarbons.

**EXPERIMENT**

**Catalyst Preparation**

A pore-filling incipient wetness impregnation (IWI) method was used to prepare Fe, Cu monometallic, and Fe-Cu bimetallic catalysts by adding an aqueous solution of Fe(NO3)3·9H2O (Aldrich, 99.99%) and Cu(NO3)2·2.5H2O (Alfa Aesar ≥98%) onto the γ-alumina (Sasol PURALOX TH 100/150) support. The total metal loading (Fe + Cu) was kept at 15 wt% (based on the support weight). To obtain the desired Cu/(Fe + Cu) atomic ratios, the Fe and Cu concentrations were adjusted. After impregnation, the catalysts were dried at 383 K for 3 h and then calcined in an electric furnace at 673 K for 2 h. The detailed procedure was reported elsewhere (Wang et al., 2018). The K-promoted catalysts were prepared by using a sequential impregnation in two steps. First, K was impregnated onto the alumina support using K2CO3 aqueous solution, which was dried at 383 K overnight. Then Fe and Cu were co-impregnated on the K-loaded alumina support using the mixed Fe and Cu aqueous solution, followed by drying and calcination under the same conditions. The Cu/(Fe + Cu) atomic ratios varied in the range of 0.0–1.0. The catalysts are termed as Fe-Cu(X)/K(Y)/Al2O3, where X and Y represent the Cu/(Fe + Cu) and K/Fe atomic ratios, respectively.

**Activity Test**

CO2 hydrogenation was carried out in a high-temperature and high-pressure fixed-bed flow reactor system. Typically, about
0.2 g of catalyst mixed with amorphous SiO$_2$ (75–250 μm particle size, about 0.5 g) was loaded into a stainless-steel tube, which had an internal diameter of 6 mm (The catalyst bed volume was about 1.2 cm$^3$). The catalyst was pretreated at 673 K with H$_2$ (50 ml min$^{-1}$) for 2 h. After cooling down to 573 K, the feed gas, CO$_2$/H$_2$/Ar (24/72/4, vol%), 99.999%) was then introduced and the system pressure was increased to 1.1 MPa (GHSV = 3600 ml g$^{-1}$ cat$^{-1}$ h$^{-1}$). The reactor system was maintained at 573 K for the catalytic reaction. The gas flow rate and reactor pressure were regulated with mass flow controllers and a backpressure regulator, respectively. An Agilent 3000 Micro-GC with TCD was used for the online analysis of gas products including Ar, CO, CH$_4$, and CO$_2$ while the gas-phase hydrocarbon products were denoted as 

Catalyst Passivation 

After CO$_2$ hydrogenation at 573 K and 1.1 MPa for 20 h, the catalyst was cooled down to 298 K under the feed gas and subsequently passivated with 1 vol% O$_2$/He (purity >99.999%) at a flow rate of 30 ml min$^{-1}$. The area of O$_2$ peak in the effluent measured by the Agilent Micro-GC-TCD was used as an indicator for the catalyst passivation. When the O$_2$ peak area became constant, the catalyst passivation was complete. Then the catalyst was collected for characterization, which hereafter is denoted as spent catalyst. Freshly reduced catalysts after the typical H$_2$-pretreatment procedure were also preserved through the same passivating procedure, which are denoted as reduced catalysts.

Catalyst Characterization 

Hydrogen Temperature-Programmed Reduction 

Hydrogen temperature-programmed reduction (H$_2$-TPR) was carried out at ambient pressure using a Micromeritics AutoChem 2910 instrument. About 100 mg of catalyst was loaded in a U-shaped quartz tube reactor (held by quartz wool). To remove the adsorbed species on the surface, the catalyst was pretreated at 393 K (10 K min$^{-1}$) under Ar (purity >99.999%, 25 ml min$^{-1}$) for 1 h prior to reduction. After being cooled down to 323 K, the carrier gas was subsequently switched to 10 vol% H$_2$/Ar at 20 ml min$^{-1}$ and sustained throughout the analysis. After a stable baseline was established, the temperature program was started by increasing the temperature to 1173 K at a ramp of 10 K min$^{-1}$ and then maintained at 1173 K for 30 min. For the quantitative analysis of the H$_2$ consumption, the TCD signal was calibrated with the standard Ag$_2$O powder (100%).

Fe K-Edge X-Ray Absorption Spectroscopy 

Fe K-edge x-ray absorption spectroscopy (XAS) was performed at the insertion-device beamline of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source (APS), Argonne National Laboratory. In brief, the X-ray passed through a cryogenically cooled double-crystal Si (111) monochromator in conjunction with an uncoated glass mirror to minimize the presence of higher harmonics, and focused onto the sample. The XAS data were collected in a transmission mode using I$_0$ and I ionization chambers filled with N$_2$/He and 20% Ar/ N$_2$, respectively.

In situ measurements were conducted using a continuous-flow XAS reactor cell (18 in. long, 0.75 in. diam.). Calcined Fe/Al$_2$O$_3$ and Fe-Cu/Al$_2$O$_3$ catalyst samples were pressed into a cylindrical holder with a thickness chosen to give a total absorbance ($\mu_t$) at the Fe K-edge of about 2.0 and an edge step (Δ$\mu_t$) of ca. 0.5, and then reduced in a stream of H$_2$ at 673 K for 30 min followed by CO$_2$/H$_2$ at 573 K for 30 min. After treatment, X-ray absorption spectra at Fe K-edge were obtained at ambient temperature. The spectrum of the Fe foil was acquired simultaneously with those of Fe-based catalysts for energy calibration. The obtained Fe K-edge XAS was analyzed in a conventional manner including background subtraction and normalization followed by Fourier filtering. The X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data were recorded near the K-edge of Fe and treated using the Athena software package.

High Resolution Transmission Electron Microscopy 

The reduced Fe-Cu catalysts were analyzed by the transmission electron microscopy (TEM, Talos, 80 kV, FEI Company). Reduced samples were first collected after the passivation and then ultrasonically dispersed in ethanol. A few droplets of ethanol suspension were dripped onto a carbon-coated copper grid followed by drying at ambient temperature. Typically, about 30 micrographs were taken for each sample. Alloys of Fe-Cu particle size histograms were generated by counting at least 200 particles.

The morphological properties and elemental distribution of the reduced Fe-Cu catalysts were examined by the scanning transmission electron microscope in conjunction with the energy-dispersive X-ray spectroscopy (STEM/EDS) using the FEI Titan 60–300 microscope equipped with a spherical aberration corrector on the probe-forming lens at an accelerating voltage of 300 kV with a monochromatic beam and spherical aberration correction, providing sub-angstrom imaging resolution. EDS maps were acquired using a high-angle annular dark-field (HAADF) detector. A collection angle of 51–300 mrad was used for the HAADF–STEM imaging. A camera length of 115 mm, beam current of 45 pA, and beam convergence of 30 mrad were used for STEM image acquisition. The sample preparation procedure was the same as that for the TEM analysis. Noteworthy, an Au-coated molybdenum grid, with Mo washer and clip was applied instead of the traditional copper grid to avoid the interference of Cu signal from the copper grid in both mapping and quantifying.

In situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy 

The possible adsorbed surface species during CO$_2$ hydrogenation over the mono- and bi-metallic Fe-Cu catalysts were investigated by in situ DRIFTS over a Nicolet Nexus 470 spectrometer equipped with a smart collector environmental chamber. About 20 mg of sample was mounted on the chamber for each measurement. The sample was initially purged by N$_2$ (50 ml min$^{-1}$) at 373 K for 1 h, followed by the reduction in a UHP H$_2$ flow (50 ml min$^{-1}$) at 523 K (ramping rate, 10 K min$^{-1}$) for 1 h. The sample was purged again by N$_2$ at this temperature for 30 min. An
interferogram was then collected at this condition and used as the background. After that, the CO$_2$/H$_2$/Ar (24/72/4, vol%) mixture gas was introduced at a flow rate of 50 ml min$^{-1}$ to initiate the reaction. The IR spectra were then recorded at the reaction time of 10, 20, and 30 min, respectively. The spectra were acquired by 128 scans at a resolution of 4 cm$^{-1}$. OMNIC ver. 7 software was used for data collection and processing.

It should be pointed out that our target is to differentiate the formed and adsorbed species over the catalyst surface during the reaction through this series of experiments, rather than the change of the catalyst in the conditions of H$_2$/N$_2$ purge. Thus, the interferogram of the catalyst sample itself was used as the background instead of KBr.

**Temperature-Programmed Desorption**

Micromeritics AutoChem 2910 was used to perform the temperature-programmed desorption (TPD) experiments at ambient pressure. For H$_2$-TPD, typically, about 150 mg of the calcined catalyst was placed in a U-shaped quartz tube reactor and reduced at 673 K (5 K min$^{-1}$) under a 50 ml min$^{-1}$ H$_2$ flow (purity >99.999%) for 2 h. The reactor was then cooled down to 200 K under H$_2$ flow using an isopropanol-liquid-N$_2$ mixture to prevent desorption of weakly adsorbed hydrogen. To remove H$_2$ gas remained within the reactor and the gas line, the system was then purged with 0.95 vol% Ar/He flow (purity >99.999%, 30 ml min$^{-1}$) to remove residual gaseous H$_2$. When the H$_2$ pressure (observed from an on-line mass spectrometer) became constant, the H$_2$-TPD experiment was performed by raising the reactor temperature from ~280 to 1173 K at a ramp of 10 K min$^{-1}$ under 0.95 vol% Ar/He (purity >99.999%) flow (30 ml min$^{-1}$). Here, Ar was used as an internal standard for the quantitative analysis of the effluent gas detected by an on-line mass spectroscopy (AMETEK Dycor Dymaxion Mass Spectrometer DM200M).

In CO$_2$-TPD, after the catalyst was reduced at 673 K, the temperature was reduced to 573 K under H$_2$ flow, and then the catalyst was purged with 0.95 vol% Ar/He (purity >99.999%, 30 ml min$^{-1}$) for 30 min. CO$_2$ adsorption was then performed at 573 K by introducing 12 vol% CO$_2$/He mixture gas at a flow rate of 30 ml min$^{-1}$ for 1 h, followed by cooling down to room temperature. The catalyst was purged with 0.95 vol% Ar/He (purity >99.999%, 30 ml min$^{-1}$) again to remove any trace of gaseous CO$_2$ until CO$_2$ pressure became constant as indicated by the mass spectrometer. The CO$_2$-TPD experiment was carried out using the same procedure as that for H$_2$-TPD.

**RESULTS AND DISCUSSIONS**

**Reducibility of Supported Fe-Cu Catalysts**

The H$_2$-TPR profiles of the calcined Fe-Cu/Al$_2$O$_3$ catalysts with different Cu/(Fe + Cu) atomic ratios are shown in Figure 1. A major reduction peak was observed at 604 K for the calcined Fe/Al$_2$O$_3$ catalyst along with two smaller peaks at 735 and 961 K. The reduction of iron oxide usually involves three sequential steps of Fe$_2$O$_3$ to Fe$_3$O$_4$, Fe$_3$O$_4$ to FeO, and FeO to metallic Fe (Lögdberg et al., 2009; Jozwiak et al., 2007), occurring at different temperatures. The reduction temperatures can also vary with the particle size, morphology, and the interaction between iron oxide phase and the alumina support. Nonetheless, the two smaller peaks at higher temperatures (735 and 961 K) and its low degree of reduction (41%, Figure 2) indicates the strong interaction between iron oxide and Al$_2$O$_3$ support in the calcined Fe catalyst, resulting in the formation of large amount of reduction-resistant Fe-Al-O species (Lögdberg et al., 2009).

With the addition of Cu, all the reduction peaks of Fe-Cu(X)/Al$_2$O$_3$ catalysts shifted to lower temperature. The more Cu amount, the lower reduction temperature. It suggests that the addition of Cu made the reduction of iron oxide easier. It is worth mentioning that the reduction peaks of Fe-Cu(0.75)/Al$_2$O$_3$ sample located at lower temperatures than those for the Cu/
Figure 2 shows the DR as a function of the Cu/(Fe + Cu) atomic ratio. The DR increased with the increase of Cu content in the catalyst (the blue line). Because the Cu/Al2O3 catalyst itself had a high DR of 98.8%, the increased DR could be attributed to Cu alone and/or the synergistic effect of Fe and Cu. Assuming there was no interaction between Fe and Cu, we could calculate the DR for each Fe-Cu(X)/Al2O3 sample by adding their corresponding DRs in proportion to their composition (the black line). Obviously, all the measured DRs of Fe-Cu(X)/Al2O3 samples were higher than the sum of the individual DR contribution from Cu and Fe-Cu synergy when combining Fe and Cu in the Fe-Cu(X)/Al2O3 catalyst, especially to that of the Fe-Cu(0.17) sample, which contains more Fe content than Fe-Cu(0.5) sample.

The degree of reduction (DR) as a function of atomic Cu/(Fe + Cu) ratio for Fe-Cu(X)/Al2O3 catalysts measured by H2-TPR. The results reveal that iron oxide was not reduced to Fe0 under the conditions used for the XAS analysis.

As shown in Supplementary Figure S1, the peak in the pre-edge region of the reduced Fe-Cu(0.17)/Al2O3 was broadened relative to that of the reduced Fe/Al2O3 catalyst at 7,114.4 eV. The peak in the pre-edge region of Fe-Cu(0.17)/Al2O3 shifted to lower energy, while there was also an increase in intensity at higher energy. This shift suggests that there was a small amount of metallic Fe in the reduced Fe-Cu(0.17)/Al2O3 catalyst. Similar changes in the pre-edge region occurred for reduced Fe-Cu(0.5)/Al2O3, but with less contribution from metallic Fe. It is consistent with the catalyst composition where the Fe-Cu(0.17) sample contains more Fe content than Fe-Cu(0.5) sample.

Similar to the XANES profiles, the EXAFS spectra in Figure 3B also suggests that the reduced Fe/Al2O3 catalyst was more like Fe2O3. It had an Fe-O peak (phase uncorrected distance) at 1.47 Å, and an Fe-O-Fe scattering peak at 2.82 Å (phase uncorrected distance). Over the reduced Fe-Cu(0.17)/Al2O3 catalyst, besides the Fe-O and Fe-O-Fe(Cu) distances, a new distance of 2.36 Å emerged, which can be assigned to the metallic Fe-Fe(Cu) distance. It is a clear evidence showing that the addition of Cu increased the reduction degree of Fe in the Fe-Cu bimetallic catalyst. Similarly, the radial distances from the reduced Fe-Cu(0.5)/Al2O3 catalyst were not much different from the reduced Fe-Cu(0.17)/Al2O3 catalyst, implying that the types of the reduced elements are similar, but the amounts are different likely due to the difference in the Fe-Cu compositions.
FIGURE 3 | (A) Fe K-edge XANES spectra and (B) \( k^3 \)-weighted EXAFS Fourier-transform magnitude spectra of the Fe/Al2O3, Fe-Cu(0.17)/Al2O3, Fe-Cu(0.5)/Al2O3 catalysts and the reference samples.

FIGURE 4 | TEM images of the reduced Fe-Cu(0.17)/Al2O3 with different magnifications (A–C) and its particle size distribution based on approximately 200 particles of TEM image (D).
mainly lied in the range of 4–7 nm (Figure 4D). The lattice space was measured to be 2.01 Å and 2.53 Å (Figure 4C), which corresponds to FeCu alloy (110) and Fe₃O₄ (311) (Omar, 2016; Wei et al., 2017), respectively. The alloy lattice space matches the d-spacing of the FeCu alloy from the XRD results reported in our prior work (Wang et al., 2018). It should be noted that the d-spacing values for the Fe-Cu alloys are similar. Additionally, according to the binary phase diagrams of Fe and Cu, there is no specific ratio of Fe and Cu in alloys. Thus, it is impossible to distinguish them both in XRD and TEM.

The presence of Fe-Cu alloy particles was also confirmed by Z-contrast in the high-angle annular dark-field image (HAADF) of the reduced Fe-Cu(0.17)/Al₂O₃ catalyst as shown in Figure 5. The corresponding EDS mapping images for Al, O, Fe, and Cu elements are shown in Supplementary Figure S2. Both Al and O species distributed uniformly across the sample island, while Fe and Cu species existed in close proximity but at different relative concentrations. Evidently, Fe and Cu were well-dispersed, which is consistent with the observations from the TEM images. Comparing the Fe and Cu distributions, we observed that most Fe and Cu elements were located at the same places, especially at the large Fe areas, indicating the combination of Fe and Cu. It was further confirmed by measuring the d-spacing. The magnified inset in Figure 5A shows a representative particle with a relatively clear lattice fringe alignment. The measured average d-spacing was ca. 2.01 Å, which is in accordance with the results from both TEM images and XRD patterns (Wang et al., 2018). Thus, these particles are representative Fe-Cu alloy particles.

To confirm the alloy formation, these eight representative alloy particles (with the d-spacing = 2.01 Å) in the HADDF and EDS images (the same area of TEM images) were scanned by the energy-dispersive X-ray spectroscopy mapping technique in STEM mode (STEM/EDS). This technique allows for the identification of the elemental compositions of individual bimetallic nanoparticles on the catalyst surface. Their compositions are listed in Table 1. The Cu/(Fe + Cu) ratios were in the range of 0.17–0.48, more centered between 0.2 and 0.3 with the mean at 0.29. It is consistent with the best Cu/(Fe + Cu) ratio for the Fe-Cu alloy composition suggested by the DFT simulation (Nie et al., 2016; Nie et al., 2017).

Therefore, the STEM/EDS results demonstrated a uniform distribution of Fe and Cu in the nanosized alloy particles after reduction, which is in good agreement with the XRD results over the same sample (Wang et al., 2018).

### Surface Adsorbed Species

To investigate the surface species on the bimetallic Fe-Cu catalysts during CO₂ hydrogenation, in situ diffuse reflectance FT-IR spectra were recorded after the CO₂ hydrogenation reaction was initiated at 523 K and atmospheric pressure for 30 min. Before the reaction, all samples were reduced with pure CO at 523 K and 1 atm for 1 h.

![Figure 5](image)

**Figure 5** (A) HAADF STEM image of the reduced Fe-Cu(0.17)/Al₂O₃ catalyst and (B) corresponding STEM/EDS overlap maps for Fe and Cu elements.

| Particle # | Analyzed composition / at. % | Cu/(Fe + Cu) atomic ratio / at.at⁻¹ |
|------------|-----------------------------|-------------------------------------|
|            | Fe | Cu |                                 |
| 1           | 22.27 | 4.62 | 0.17 |
| 2           | 4.66 | 1.72 | 0.27 |
| 3           | 25.06 | 7.34 | 0.23 |
| 4           | 5.76 | 2.69 | 0.32 |
| 5           | 4.09 | 2.30 | 0.38 |
| 6           | 4.42 | 4.02 | 0.48 |
| 7           | 5.66 | 2.46 | 0.30 |
| 8           | 10.70 | 2.22 | 0.17 |

*Uncertainty of each element in quantitative analysis: Fe (0.09 at.%); Cu (0.02 at.%); C (0.31 at.%); Al (0.10 at.%); O (0.21 at.%).
H₂ at 523 K for 1 h. The obtained DRIFT spectra are shown in Figure 6.

As seen, IR bands at 1,377, 1,634, 1,760, 1,942, and 2,120 cm⁻¹ were observed within the range of 1,200–2,200 cm⁻¹ over the Fe-Cu(0.17) catalyst, while the Fe-Cu(0.5) sample displayed the IR bands at 1,525, 1,646, 1,760, and 1,942 cm⁻¹. The bands at 1,634 and 1,646 cm⁻¹ can be attributed to the adsorbed bicarbonates with different vibrational modes (Busca and Lorenzelli, 1982; Rethwisch and Dumesic, 1986; Gopal et al., 1987), while the 1,525 cm⁻¹ IR band is the characteristic of carbonates (Peri, 1966; Parkyns, 1971; Morterra and Orío, 1990; Turek et al., 1992; Morterra and Magnacca, 1996). These IR bands confirm the formation of adsorbed bicarbonate and carbonate species on both bimetallic Fe-Cu catalysts during CO₂ hydrogenation. The 1,942 and 2,120 cm⁻¹ bands can be attributed to the adsorbed CO species (Bando et al., 1997; Hadjiivanov et al., 2001), which were not observed on either Cu/Al₂O₃ or Fe/Al₂O₃ catalysts. It indicates that the combination of Fe and Cu promoted the RWGS reaction, generating more adsorbed CO species. Although Cu/Al₂O₃ can promote the RWGS reaction, the formed CO species are quickly released into the gas phase due to the weak interaction between Cu and CO. As a result, such two bands were not observed over the Cu/Al₂O₃ catalyst.

Besides, the IR bands at 1,377, 2,854, and 2,932 cm⁻¹ represent different vibrational modes of adsorbed formate species (Millar et al., 1991; Clarke and Bell, 1995; Cabilla, 2003) and the 1,760 cm⁻¹ IR band is the characteristic of formic acid (Shimanouchi, 1972). The observation of the adsorbed formate and formic acid species provides an evidence for one potential CO₂ hydrogenation pathway on the bimetallic Fe-Cu/Al₂O₃ catalysts that the reaction could go through a direct hydrogenation via formate, then formic acid as main intermediates to C₂⁺ hydrocarbons, which was also proposed on the basis of DFT simulation (Nie et al., 2016; Nie et al., 2017).

The intensities of these IR bands on the Fe-Cu(0.17) catalyst were much stronger than those of the Fe-Cu(0.5) catalyst, indicating that the Fe-Cu synergy in the Fe-Cu(0.17) catalyst is stronger than that in the Fe-Cu(0.5) catalyst in terms of CO₂ hydrogenation. It is in good agreement with H₂-TPR results shown in Figure 2. On the contrast, the Fe/Al₂O₃ catalyst only showed a broad IR peak at 1,300–1,700 cm⁻¹ along with a band at ~2,932 cm⁻¹.

Besides the IR spectra after 30 min of CO₂ hydrogenation reaction, we also recorded the DRIFT spectra at different reaction time including 10, 20, and 30 min over the Fe-Cu(0.17)/Al₂O₃ catalyst, which is shown in Supplementary Figure S3. No change was detected in these spectra, revealing that the adsorbed species are stable.

### H₂ Adsorption Properties

Figure 7 shows the H₂-TPD profiles of the reduced Fe/Al₂O₃, Fe-Cu(0.17)/Al₂O₃, Fe-Cu(0.5)/Al₂O₃, and Cu/Al₂O₃ catalysts. The H₂-TPD profile of the Al₂O₃ support is also presented as the baseline. Their direct comparison is presented in Supplementary Figure S4. The H₂ desorption on the reduced Fe/Al₂O₃ catalyst mainly occurred at 800 K with several minor desorption peaks at...
440, 584, and 1030 K. The H\textsubscript{2}-TPD profiles of the Fe-Cu bimetallic catalysts generally showed similar features to that of the monometallic Fe catalyst, suggesting the reduced iron sites are responsible for H\textsubscript{2} adsorption on the Fe-Cu catalyst surface. Compared to the Fe/Al\textsubscript{2}O\textsubscript{3} catalyst, the combination of Fe and a small amount of Cu (X\textsubscript{Cu}/Fe = 0.17) enhanced the H\textsubscript{2} desorption at 800 K. Upon further increasing the Cu content to X\textsubscript{Cu}/Fe = 0.5, however, the H\textsubscript{2} desorption peak at 800 K became smaller. On the other hand, the desorption peak at 380–600 K was much promoted with the increase of Cu amount. Interestingly, the H\textsubscript{2}-TPD profile of the reduced Cu/Al\textsubscript{2}O\textsubscript{3} catalyst was significantly different from those of the Fe-based catalysts, but close to that of the Al\textsubscript{2}O\textsubscript{3} support, suggesting that Cu has low ability in H\textsubscript{2} adsorption. The H\textsubscript{2} desorption in the range of 600–900 K on the Cu catalyst was negligible.

To quantitatively analyze the H\textsubscript{2} adsorption amount, the H\textsubscript{2}-TPD peaks were deconvoluted using 50% Gaussian plus 50% Lorentzian functions. As shown in Figure 8 with the reduced Fe-Cu(0.17)/Al\textsubscript{2}O\textsubscript{3} catalyst as a typical example, the final curve generated from the summation of the deconvoluted peaks fitted the experimental data well. The deconvoluted peaks were arbitrarily denoted as I-IV from low to high temperature, representing four different types of adsorbed hydrogen species on the catalyst surface. Types I and II represent the weakly adsorbed H\textsubscript{2} at lower temperatures (below 600 K), which can be ascribed to atomic hydrogen adsorbed on the metal surface (Bozso et al., 1977). While the H\textsubscript{2} desorption observed at higher temperatures (>600 K, type III as moderately adsorbed H\textsubscript{2} and type IV as strongly adsorbed H\textsubscript{2}) are the H\textsubscript{2} species adsorbed on the metallic Fe\textsuperscript{0} and/or Fe-Cu alloy surface decorated with unreduced metal oxide (Zowtiak and Bartholomew, 1983; Bartholomew, 1990).

Based on the peak deconvolution, we were able to quantitatively estimate the amount of different types of adsorbed H\textsubscript{2} by integrating each peak, which are listed in Supplementary Table S1 for all Fe-Cu(X)/Al\textsubscript{2}O\textsubscript{3} samples. Figure 9A shows the amounts of type III + IV adsorbed H\textsubscript{2} on the Fe-Cu(X)/Al\textsubscript{2}O\textsubscript{3} catalysts. Adding a small amount of Cu greatly promoted the amount of type III + IV adsorbed H\textsubscript{2}, especially at the Cu/(Fe + Cu) atomic ratio of 0.10 and 0.17, the amount of type III + IV adsorbed H\textsubscript{2} of which was 238.1 and 240.0 \textmu mol g\textsuperscript{-1} cat\textsuperscript{-1}, respectively, about 50% higher than that of the Fe/Al\textsubscript{2}O\textsubscript{3} catalyst. Further increasing Cu content, however, resulted in the decrease of type III + IV adsorbed H\textsubscript{2}. When the Cu/(Fe + Cu) ratio was 0.75, the amount of type III + IV adsorbed H\textsubscript{2} became 113.5 \textmu mol g\textsuperscript{-1} cat\textsuperscript{-1}, which was even lower than that of the Fe/Al\textsubscript{2}O\textsubscript{3} catalyst. Such a trend is consistent with the change in the Fe-Cu synergy characterized by the degree of reduction of the Fe-Cu catalyst with the addition of Cu shown in Figure 2.

We then correlated the space-time yield (STY) of C\textsubscript{2}+ hydrocarbons with each type of adsorbed H\textsubscript{2} species. The amount of moderately plus strongly adsorbed H\textsubscript{2} (type III + IV) showed a good relationship with C\textsubscript{2}+ hydrocarbons production (Figure 9B). Such a strong correlation evidently
displays that the moderately and strongly adsorbed H₂ species played an important role in the formation of C₂⁺ hydrocarbons. In other words, the Fe-Cu synergy in CO₂ hydrogenation could be attributed to the enhancement in H₂ adsorption induced by the combination of Fe and Cu.

**CO₂ Adsorption Properties**

The effect of Fe-Cu combination on the CO₂ adsorption properties of the reduced Fe-Cu(X)/Al₂O₃ catalysts was examined by CO₂-TPD, which is presented in Figure 10. The γ-Al₂O₃ support was also evaluated as a reference. It showed a CO₂ desorption peak at 350 K, which is known as the decomposition of the surface bicarbonate species (Pan et al., 2008). Over the monometallic Fe catalyst, another strong CO₂ desorption peak was observed at around 480 K, which can be ascribed to the decomposition of the surface carbonate species (Pan et al., 2008). With the addition of Cu, another new small CO₂ desorption peak at 550–700 K emerged over the Fe-Cu bimetallic catalysts, which can be referred to the bidentate carbonate species (Pan et al., 2008). The observed bicarbonate and carbonate species are in a good agreement with the DRIFTS results. In contrast, the monometallic Cu catalyst exhibited a similar profile to the γ-Al₂O₃ support, indicating that Cu itself does not contribute to CO₂ adsorption. Therefore, the new peak induced by the addition of Cu could be attributed to the Fe-Cu strong interaction and/or Fe-Cu alloys. Correlating to CO₂ hydrogenation performance, it also suggests that the observed Fe-Cu synergy is because the combination of Fe and Cu enhanced CO₂ adsorption.

It is projected that the addition of K could greatly enhance CO₂ adsorption due to its basic nature. Consequently, we also examined the CO₂ desorption behavior of K-promoted catalysts, i.e., the Fe-Cu(0.17)/K(Y)/Al₂O₃ catalysts. As shown in Figure 11A, compared to the Fe-Cu(0.17) catalyst, the addition of K increased all types of the adsorbed CO₂ species with desorption peaks at around 350 K, 450 K, and 550–700 K. Additionally, a new desorption peak at higher temperatures (>700 K) emerged, which could be ascribed to the adsorbed bicarbonate and carbonate species.
CO₂ on potassium ferrite (K₂Fe₂O₄) (Zowtiak and Bartholomew, 1983). Similar desorption peak after K addition was also observed on the Fe-Zn-K catalysts (Zhang et al., 2015).

To find out the relationship between the adsorbed CO₂ species and CO₂ hydrogenation reaction, the desorption profiles of the Fe-Cu(0.17)/K(Y)/Al₂O₃ catalysts were deconvoluted and quantitatively analyzed. Using the Fe-Cu(0.17)/K(0.3)/Al₂O₃ catalyst as an example (Figure 11B), four peaks denoted as types I–IV were identified from low to high temperatures, suggesting four different CO₂ adsorption states on the catalyst surface. The quantities of deconvoluted peaks for all CO₂-TPD profiles are summarized in Supplementary Table S2.

As described above, the moderately adsorbed CO₂ (Type III at 550–700 K) is related to the Fe-Cu interaction. The addition of K changed the moderately adsorbed CO₂, suggesting that K also interacted with Fe and Cu. In addition, it is responsible for the emergence of strongly adsorbed CO₂ (Type IV at 600–900 K), as no such peak was observed over the corresponding catalyst without K addition. It is mainly because K could increase the surface basicity by donating the electron to the Fe-based catalyst (i.e., acting as an electronic promoter) (Dorner et al., 2010). Thus, we correlated the STY of C₂⁺ hydrocarbons with each type of adsorbed CO₂. It was found that the C₂⁺ hydrocarbons production rate is dependent on the amount of moderately plus strongly adsorbed CO₂ (type III + IV) (Supplementary Figure S6). It suggests that the moderately and strongly adsorbed CO₂ may be responsible for the formation of C₂⁺ hydrocarbons. It also means the Fe-Cu synergy comes from the Fe-Cu strong interaction, which enhances CO₂ adsorption (both amount and strength) on the catalyst surface.

**Effect of H₂ and CO₂ Adsorption Properties on Olefin Formation**

In CO₂ hydrogenation, we observed that the olefin selectivity increased significantly with the addition of K, resulting in an increased O/P (olefin/paraffin) ratio, which may be related to the change in the H₂ and CO₂ adsorption properties of the catalysts with K. Consequently, the H₂-TPD experiments were also performed over the Fe-Cu(0.17)/K(Y)/Al₂O₃ catalysts, and the results are presented in Supplementary Figure S5. The quantitative results via peak deconvolution are listed in Supplementary Table S1. Adding a small amount of K (K/Fe = 0.3) enhanced H₂ adsorption on Fe-Cu(0.17) catalyst, especially the weakly adsorbed H₂, due likely to the electronic enhancement of K to metals. However, further increasing K content (K/Fe = 0.5 and 1.0) resulted in the decrease of the moderately and strongly adsorbed H₂, due likely to that overloaded K could cover the metal surface for H₂ adsorption.

As discussed in the H₂ adsorption properties and CO₂ adsorption properties sections, both the moderately and strongly adsorbed H₂ species (Type III + IV) and the moderately and strongly adsorbed CO₂ (Type III + IV) showed good relationship to the formation of C₂⁺ hydrocarbons. On the other hand, in CO₂ hydrogenation, the production of paraffins requires more H₂ than olefins. Hence we used the ratio of the amount of the moderately and strongly adsorbed CO₂ over the amount of the moderately and strongly adsorbed H₂ to correlate with the olefin/paraffin ratio (O/P) obtained from CO₂ hydrogenation over the Fe-Cu(0.17)/K(Y)/Al₂O₃ catalysts. The result is presented in Figure 12.

![Graph](image-url)
Here we observed a clear and very strong relationship between the O/P ratio and the ratio of the amount of the moderately and strongly adsorbed CO$_2$ over the amount of the moderately and strongly adsorbed H$_2$ with the R-square value of more than 0.99. It reflects that both the moderately and strongly adsorbed CO$_2$ and H$_2$ played a critical role in determining the olefin selectivity in CO$_2$ hydrogenation. In other words, it is possible to obtain more olefins than paraffins by controlling the ratio of the moderately and strongly adsorbed CO$_2$ over the moderately and strongly adsorbed H$_2$ when we design a proper catalyst for CO$_2$ hydrogenation to higher hydrocarbons.

When we compared the Fe-Cu catalyst with relevant studies of Fe-based catalyst, we found that this CO$_2$/H$_2$ adsorption behavior is the key to light olefin formation. For instance, Zhang et al. reported a promotion of Fe-Zn-K catalyst on CO$_2$ conversion, but they reported Zn addition had almost no effect on light olefin selectivity. And they also found that adding Zn decreased CO$_2$ uptake (Zhang et al., 2015). These results proved that Zn acted more like a structural promoter that can help Fe to be better dispersed and reduced. It is not an actual synergetic effect. We will further discuss the importance of light olefin formation and its role in the whole CO$_2$ hydrogenation process in next section.

The comprehensive investigation on the relationship between the adsorbed CO$_2$ and H$_2$ species and the catalyst activity and product selectivity shall thus be conducted to improve our fundamental understanding of CO$_2$ hydrogenation to higher hydrocarbons over the Fe-Cu bimetallic catalysts.

**Pathways of CO$_2$ Hydrogenation**

To investigate the pathways of CO$_2$ hydrogenation, the Fe-Cu(0.17)/K(0.3)/Al$_2$O$_3$ catalyst was tested over a wide range of residence time (W/F) at 573 K and 1.1 MPa. The CO$_2$ conversion as a function of W/F is shown in Supplementary Figure S7. Clearly, the CO$_2$ conversion increased with increasing the residence time and gradually became constant at high W/F values.

**Figure 13** shows the CO, CH$_4$, and C$_2^+$ hydrocarbons selectivities as a function of CO$_2$ conversion. With the increase of CO$_2$ conversion, the CO selectivity decreased while the selectivity of C$_2^+$ hydrocarbons increased, indicating that CO is a primary product while C$_2^+$ hydrocarbons are produced from CO, probably via a process similar to FTS (Riedel et al., 2001). It is noticed that at the CO$_2$ conversion less than 10%, the CO selectivity, CH$_4$ selectivity, and C$_2^+$ hydrocarbons selectivity were almost constant at 90, 4, and 6%, respectively. It hints that small parts of CH$_4$ and C$_2^+$ hydrocarbons may come from direct hydrogenation of CO$_2$ without through CO intermediate (Riedel et al., 2001). In addition, CH$_4$ selectivity did not change much with the increase of CO$_2$ conversion whereas the CO selectivity decreased sharply, suggesting that CH$_4$ formation is not closely related to CO formation.

Among the C$_2^+$ hydrocarbons, the paraffin selectivity increased drastically with the increase of CO$_2$ conversion, while the olefin selectivity only increased a bit, leading to a rapid decrease in the C$_2$-C$_4$ olefin/paraffin ratio (**Figure 14**). It suggests that light olefins could be the primary product from CO$_2$ hydrogenation, and then are further hydrogenated to paraffins. Hence, to achieve olefin-rich hydrocarbons, it would be crucial to suppress the consequent hydrogenation of olefins by tailoring the surface coverage of CO$_2$ and H$_2$ in CO$_2$ hydrogenation.

**CONCLUSION**

This work focused on catalyst characterizations to better understand the Fe-Cu synergistic effect in CO$_2$ hydrogenation, where the Fe-Cu(0.17) catalyst showed the best performance. Adding Cu to Fe promoted the reduction of iron oxide to Fe$^0$ and the formation of Fe-Cu alloy as evidenced by H$_2$-TPR, high resolution TEM, and XAS. It also influenced the adsorbed surface species during CO$_2$ hydrogenation as observed by in situ DRIFTS. Furthermore, the addition of Cu promoted the adsorption of the moderately and strongly adsorbed H$_2$ species and moderately adsorbed CO$_2$ species, which were responsible for the increased CO$_2$ conversion and C$_2^+$ selectivity. Adding K
further increased the moderately and strongly adsorbed CO₂, but slightly reduced the moderately and strongly adsorbed H₂, resulting in an increased adsorbed-CO₂/adsorbed-H₂ ratio and consequently producing olefin-rich hydrocarbons with a significantly increased O/P ratio. Both the in situ DRIFTS and the product distribution analysis suggested that C₂⁺ hydrocarbons were largely produced from consequent reduction of CO via the FT-like process, along with a small portion formed via a direct CO₂ hydrogenation pathway.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding authors.

AUTHOR CONTRIBUTIONS

CS, XW, and WW contributed to conception and design of the study. GZ conducted the XAS analysis, KW and FZ performed the TEM analysis and WW completed all other experiments. WW wrote the first draft of the manuscript. All authors contributed to data analysis and visualization, manuscript revision, read, and approved the submitted version.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fceng.2021.708014/full#supplementary-material

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