Interfacial Fe$_5$C$_2$-Cu catalysts toward low-pressure syngas conversion to long-chain alcohols

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Long-chain alcohols synthesis (LAS, C$_5$+OH) from syngas provides a promising route for the conversion of coal/biomass/natural gas into high-value chemicals. Cu-Fe binary catalysts, with the merits of cost effectiveness and high CO conversion, have attracted considerable attention. Here we report a nano-construct of a Fe$_5$C$_2$-Cu interfacial catalyst derived from Cu$_4$Fe$_1$Mg$_4$-layered double hydroxide (Cu$_4$Fe$_1$Mg$_4$-LDH) precursor, i.e., Fe$_5$C$_2$ clusters (~2 nm) are immobilized onto the surface of Cu nanoparticles (~25 nm). The interfacial catalyst exhibits a CO conversion of 53.2%, a selectivity of 14.8 mol% and a space time yield of 0.101 g g$_{\text{cat}}^{-1}$ h$^{-1}$ for long-chain alcohols, with a surprisingly benign reaction pressure of 1 MPa. This catalytic performance, to the best of our knowledge, is comparable to the optimal level of Cu-Fe catalysts operated at much higher pressure (normally above 3 MPa).
long-chain alcohols, containing more than five carbons, are key alternative fuels and feedstock to manufacture plasticizers, dyes, and lubricants.\textsuperscript{14} Synthesis of long-chain alcohols (LAS) from syngas by a tandem strategy provides a facile, economical, and environment-friendly approach.\textsuperscript{1-7} Among various binary catalyst systems (Cu–Fe\textsuperscript{1,3,8}, Cu–Co\textsuperscript{9,10}, Co–Mo\textsuperscript{11,12}), Cu–Fe binary candidates have attracted considerable attention in the production of long-chain alcohols. Previous studies on Cu–Fe binary catalysts show that a yield of long-chain alcohol as high as 0.014–0.144 g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1} could be reached, albeit a relatively harsh reaction condition (3–8 MPa) is normally required. However, there is still room for the optimization of long-chain alcohols selectivity; more importantly, it is pivotal to develop catalyst system that works under mild reaction conditions.\textsuperscript{13,18-7}

Especially, the low pressure in practical operation gives a significant reduction in pressure drop, energy, and facility costs, which takes merits of both environmental and economic benefits.\textsuperscript{5,24}

To achieve this goal, a precise control over the type, dimension, and nature of Cu/Fe interface plays a key role in the production of LAS. Maintaining a high degree of Cu–Fe interface is decisive for shifting the products from hydrocarbons to long-chain alcohols. We have demonstrated previously that Fe\textsubscript{5}C\textsubscript{2} is very active for CO dissociation and C–C bond propagation, and thus is an excellent catalyst for the FTs reaction.\textsuperscript{25-27} Lu et al. recently synthesized a 3DOM FeCu catalyst with atomic steps on the Cu surface involving planar defects and lattice strain, which showed excellent performance toward higher alcohols synthesis.\textsuperscript{3,16} If we can prepare a highly dispersed iron carbide species over Cu, where CO is activated but not dissociated, it is possible to largely enhance the density of interface sites. This may render an optimized rate of C–C bond propagation on iron carbide sites and Co insertion on Cu/Fe\textsubscript{2}C\textsubscript{2}C\textsubscript{2} interface sites, and thus a high selective toward long-chain alcohols would be achieved. Layered double hydroxides (LDHs), with unique structure that metal cations are distributed in the hydroxide layers at an atomic level, have attracted extensive attention as catalyst precursors for higher alcohols synthesis.\textsuperscript{10,15,18,28,29}

In this report, we used Cu–Fe–LDHs as a precursor. After a structural topological transformation followed by an activation treatment\textsuperscript{30-34}, Fe\textsubscript{5}C\textsubscript{2} cluster supported on Cu particle catalyst is obtained. Fe\textsubscript{5}C\textsubscript{2} clusters (~2 nm) are highly dispersed over the surface of Cu nanoparticles (~25 nm) which creates rich interfacial sites; and the Cu/Fe\textsubscript{1} catalyst with optimized Fe\textsubscript{5}C\textsubscript{2}–Cu interface exhibits a CO conversion of 53.2% and space time yield of 0.101 g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1} for long-chain alcohols, at a low operation pressure (1 MPa). This is even comparable with the optimal space time yield level of other Cu–Fe binary catalysts at pressure of 3–8 MPa.

**Results and discussion**

**Catalysts synthesis and characterizations.** The Cu\textsubscript{1}Fe\textsubscript{4}Mg\textsubscript{4}–LDH precursors with different Cu/Fe molar ratios (1/1, 2/1, 4/1, and 6/1, respectively) were prepared by a nucleation and aging separation method developed previously.\textsuperscript{15} The XRD patterns (Fig. 1a) show characteristic diffractions corresponding to an LDH phase (ICPDS 14-0281); SEM images display a typical plate-like hexagonal morphology (Supplementary Fig. 1). Actually, Cu\textsubscript{4}Fe\textsubscript{1}Mg\textsubscript{4}–LDH could hardly give an LDH phase due to the strong Jahn–Teller effect of Cu\textsuperscript{2+}. The LDHs precursors were transformed to mixed metal oxides (MMO) that inherit the plate-like morphology (Supplementary Fig. 2) after thermal treatment. A CuO phase is predominant for these three samples (Fig. 1b); while the diffractions at 35.8° and 37.1° confirm the formation of CuFe\textsubscript{2}O\textsubscript{4} spinel in XRD patterns. From HRTEM images (Supplementary Fig. 3), some nanoparticles uniformly embedded in the platelet matrix are clearly observed. The CuFe\textsubscript{2}O\textsubscript{4} nanoparticles are well-dispersed near CuO nanoparticles. According to the H\textsubscript{2}-TPR measurements (Fig. 1c), the main peak shifts gradually from 280 °C to 350 °C with the increase of Cu/Fe ratio, which is ascribed to the enhanced amount of CuFe\textsubscript{2}O\textsubscript{4} spinel (a high reduction temperature) within CuO matrix (a low reduction temperature)\textsuperscript{35-37}, as confirmed by XRD (Fig. 1b) and HRTEM (Supplementary Fig. 3). The CuFe\textsubscript{4}Mg\textsubscript{4}–MMO shows the strongest interaction between CuO and CuFe\textsubscript{2}O\textsubscript{4} species in accordance with HRTEM, possibly providing the most abundant and stable interfacial structure after activation. The precursors were reduced in syngas under optimized conditions to get the supported catalysts, which were denoted as Cu\textsubscript{4}Fe\textsubscript{1}, (x/y means the ratio between Cu and Fe). The Cu\textsubscript{4}Fe\textsubscript{1} catalysts show similar XRD patterns (Fig. 1d) with metallic Cu. The average Cu particle sizes are 15.7, 18.4, 21.7, and 25.1 for Cu\textsubscript{4}Fe\textsubscript{1}, Cu\textsubscript{1}Fe\textsubscript{3}Cu\textsubscript{1}Fe\textsubscript{1}, and Cu\textsubscript{6}Fe\textsubscript{1}Fe\textsubscript{1}Fe\textsubscript{1}Fe\textsubscript{1}, respectively (Supplementary Table 1). Moreover, no obvious diffraction of Fe crystalline is resolved, which indicates that Fe species is highly dispersed in the catalyst.

**Catalytic results.** The catalysts were first evaluated under a relatively high pressure (3 MPa). Figure 2a shows the alcohol distribution over catalysts with various activation treatments (Supplementary Tables 2–6), from which both the activation atmosphere (syngas containing CO\textsubscript{2}) and the two-stage activation procedure play a vital role in tuning the synergetic effect between Cu and Fe\textsubscript{5}C\textsubscript{2}. The sample activated in syngas containing CO\textsubscript{2} (Supplementary Table 4) could slow down the rate of reduction process and facilitate carburization of Fe to produce Fe\textsubscript{5}C\textsubscript{2} species, which would maintain the tiny size of Fe\textsubscript{5}C\textsubscript{2} to form abundant Cu–Fe\textsubscript{5}C\textsubscript{2} interfacial sites. The sample reduced in syngas shows diffraction peaks of both Cu and Fe\textsubscript{5}C\textsubscript{2} phase (Supplementary Fig. 4) and rather poor catalytic behavior for the production of LA, indicating less interfacial sites merged by poor dispersion of Fe\textsubscript{5}C\textsubscript{2} is not beneficial for the production of LA. The selectivity toward long-chain alcohols enhances gradually along with the increase of Cu/Fe ratio, reaching maximum at 54.0% for Cu\textsubscript{4}Fe\textsubscript{1} at 3 MPa (specific data in Supplementary Table 7). Cu\textsubscript{4}Fe\textsubscript{1} gives out the optimal space time yield (STY) (Supplementary Table 8) toward total alcohols (0.141 g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1}) and long-chain alcohols (0.076 g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1}) at 3 MPa.

What attracts our attention most is the excellent long-chain alcohols production on Cu\textsubscript{4}Fe\textsubscript{1} under 1 MPa (Fig. 2; Supplementary Fig. 5). The Cu\textsubscript{4}Fe\textsubscript{1} has 38.6% at WHSV = 4800 mL\textsubscript{g\textsubscript{cat}}\textsuperscript{−1} h\textsuperscript{−1} with iso-conversion to other Cu\textsubscript{4}Fe\textsubscript{1} samples, although Cu\textsubscript{4}Fe\textsubscript{1} has higher value. The total alcohols yield (0.201 g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1}) of Cu\textsubscript{4}Fe\textsubscript{1} is much higher than hydrocarbons yield (0.111 g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1}), demonstrating the predominant production of alcohols rather than hydrocarbons (Supplementary Table 8). This means the high LA yield is the interplay of activity and selectivity. In addition, long-chain alcohols (C\textsubscript{5}+) (alcohols) give a higher yield than methanol (0.101 vs. 0.018 g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1}), which is among the highest level compared with previous work in Supplementary Table 9. Normally, high reaction pressure (3–8 MPa) is required for long-chain alcohols synthesis; in this work, however, a low-pressure (1 MPa) syngas conversion to long-chain alcohols is attained. Significantly, Cu\textsubscript{4}Fe\textsubscript{1} catalyst at 1 MPa reaction condition shows a satisfactory stability: 5% decrease in activity is observed within a 100 h catalytic evaluation test (Fig. 2c) and a satisfactory reproducibility (Supplementary Table 10).

To understand the outstanding catalytic performance of Cu\textsubscript{4}Fe\textsubscript{1}, the impact of catalyst synthesis on its catalytic performance was investigated. Control samples with the same Cu/Fe ratio of 4/1 synthesized through conventional impregnation and
Fig. 1 Catalysts characterizations. **a** XRD patterns of Cu₁Fe₁Mg₄-LDH precursors with three molar ratios of Cu/Fe (1:1, 2:1, 4:1, and 6:1, respectively). **b** XRD patterns of Cu₁Fe₁Mg₄-MMO calcined samples obtained from calcination of LDHs precursors. **c** H₂-TPR profiles of Cu₁Fe₁Mg₄-MMO samples. **d** XRD patterns of Cu₁Fe₁ obtained from activation of MMO samples in syngas (25% CO+25% H₂+50% CO₂) under optimum conditions (300 °C (2 h) +350 °C (1 h); rate: 2 °C min⁻¹) and passivation.

Fig. 2 Catalytic performance. **a** Alcohol distribution normalized data to total alcohols selectivity (* WHSV = 4800 mL g⁻¹ h⁻¹; b WHSV=1200 mL g⁻¹ h⁻¹; C₅+OH: long-chain alcohols, BuOH: butanol, PrOH: propanol, ETOH: ethanol and MeOH: methanol) and **b** alcohols STY at different pressures over catalysts with four Cu/Fe ratios (1/1, 2/1, 4/1, and 6/1) (reaction conditions: 27% CO+55% H₂+18% N₂; 260 °C; WHSV of 2400 mL g⁻¹ h⁻¹). **c** Time-on-stream (TOS) evolution of CO conversion over the four catalysts within 100 h test at 1 MPa. **d** Alcohols STY of Cu₄Fe₁, Cu₄Fe₁-Co, Cu₄Fe₁-im, and Cu₁₀Fe₁ at 1 MPa.
co-precipitation methods were prepared (Supplementary Fig. 6: termed as Cu$_4$Fe$_{10}$-im and Cu$_4$Fe$_1$-co, respectively), from which Cu–Fe$_2$C$_2$ interfaces were rarely observed over those conventional catalysts. However, both catalysts produced scarcely any long-chain alcohols (Supplementary Table 11), indicating the unique interfacial structure derived from the LDHs synthesis route definitely changes the catalytic activity. Another two control samples of pure Cu (denoted as Cu$_4$) or pure Fe (denoted as Fe$_1$) were prepared based on a similar LDHs approach. The Cu$_4$ sample mainly shows methanol synthesis performance and the Fe$_1$ gives conventional FTS performance (Supplementary Table 11), in accordance with previous work. When separate Cu$_4$ and Fe$_1$ catalysts were combined with various modes, long-chain alcohols could not be synthesized. This indicates that the Cu–Fe$_2$C$_2$ synergistic effect is responsible for the production of long-chain alcohols. Therefore, the synergy of interfacial sites between Fe$_2$C$_2$ and Cu is must for the long-chain alcohols (higher alcohols) synthesis from syngas. We performed further studies on samples with higher Cu/Fe molar ratios as 10:1 (termed as Cu$_{10}$Fe$_1$, Supplementary Fig. 7). Although both Cu$_9$Fe$_{10}$ and Cu$_{10}$Fe$_1$ samples have good selectivity of long-chain alcohols (Supplementary Table 12), the STY was low (Fig. 2b, d), showing that a suitable Cu/Fe ratio is important for the best catalytic performance. This suggests that catalyst with rich Cu–Fe$_2$C$_2$ interfaces derived from the LDHs precursor method could result in an excellent activity and selectivity toward long-chain alcohols even at a low reaction pressure.

**Fine structure characterizations.** To further understand the structural property of Cu$_x$Fe$_y$ catalysts, the three samples (Cu$_4$Fe$_1$, Cu$_9$Fe$_{10}$, and Cu$_4$Fe$_{10}$) were characterized by aberration-corrected scanning transmission electron microscopy (ac-STEM). For Cu$_4$Fe$_1$ and Cu$_9$Fe$_{10}$ samples (Supplementary Figs. 8, 9), the lattice fringe of Cu (111) with 0.209 nm is clearly resolved; EDS mapping images of Cu, Fe, and C demonstrate the existence of Fe$_2$C$_2$ nanoclusters on the surface of Cu nanoparticles. In the case of Cu$_4$Fe$_{10}$ sample, Fig. 3a shows the lattice fringe of Cu (111) and Fe$_2$C$_2$ (11–2); corresponding EELS mapping (Fig. 3b) illustrates the modification of Cu by Fe$_2$C$_2$ nanoclusters within a single Cu nanoparticle, which is also confirmed in another selected region in Supplementary Fig. 10. Then, quasi-in-situ STEM measurements on the used catalyst after 1 MPa syngas conversion reaction were performed (Fig. 3). The EDX-mapping results (Fig. 3c, d) also verified the homogeneous distribution of iron species on Cu. The phase of the iron species could be identified to be Fe$_2$C$_2$, as the catalyst shows sextets characteristics in Mössbauer spectrum (Supplementary Fig. 11). To further confirm the existence of iron carbide species on Cu particles, the electron energy-loss spectra (EELS) of C K-edge at the surface of Cu particle (Spot A) and support (Spot B) were studied (Fig. 3e, f). For C K-edge spectra, Spot A displays a lower energy peak relative to Spot B, accompanied by a small peak at ~280 eV, which again verifies the existence of carbide species on the surface of Cu particle.

In addition, in situ X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) experiments for Cu$_4$Fe$_{10}$-Mg$_{14}$-MMO at Cu K-edge and Fe K-edge (Fig. 4a, f) were performed to reveal the structural change during the activation treatment process to obtain Cu$_4$Fe$_1$ catalyst (in 20 mL min$^{-1}$ 5% CO+5% H$_2$+10% CO$_2$+80% He stream). The normalized Cu K-edge XANES spectra show a gradual decrease in the energy of absorption edge relative to CuO reference, accompanied with the appearance of edge features of metallic Cu, indicating a progressive reduction of CuO phase to metallic Cu. Corresponding fitting results (Supplementary Fig. 12) show that Cu species in Cu$_4$Fe$_1$ is mainly metallic Cu with rather small amount of CuO$_x$. Based on the results of previous reports and observations in this work, Cu$^0$ is regarded as active site for CO adsorption/insertion. In the Cu K-edge EXAFS spectra, initially, the coordination environment of Cu$_4$Fe$_{10}$-Mg$_{14}$-MMO is consistent with CuO, in which the peaks at 1.5 Å and 2.5 Å are assigned to the first Cu–O coordination and Cu–Cu coordination, respectively. During the activation process, the peak at 2.2 Å ascribed to Cu–Cu coordination shell gradually emerges and becomes predominant, further confirming the reduction to metallic Cu. In the case of Fe species, the normalized Fe K-edge XANES spectra show the reduction of Cu$_4$Fe$_{10}$ spinel to iron carbide phase along with the absorption edge moving to low energy. As shown in Fe K-edge EXAFS spectra, Fe–Fe coordination shell at 2.0 Å is observed at 350 °C, confirming the formation of iron carbide. Based on above results, it is concluded that the new interfacial structure is well established from LDHs precursor through refined activation process.

**Structure-performance relationship.** In addition, CO-TPD (Fig. 4g, h) was performed to quantitatively study the amount of Fe$_2$C$_2$ interfacial sites. As CO adsorption on Cu is rather weak and only be resolved through low-temperature TPD, the observed desorption peaks are ascribed to iron species. In addition to the CO desorption from iron oxide at relatively low temperature (around 300 °C, for Cu$_4$Fe$_1$) and reverse Boudouard
Fig. 4 In situ XAS measurements of Cu4Fe1 catalyst and CO-TPD measurements of Fe1, Cu4, and CuFe samples. a, e In situ XANES spectra at Cu K-edge and Fe K-edge of Cu4Fe1Mg4-MMMO in syngas treatment to obtain Cu4Fe1 catalyst (5% CO + 5% H2 + 10% CO2 + 80% He stream; 20 mL min⁻¹) at different temperatures and time points, respectively. b, f Enlarged view of absorption edge selected from (a, e). c, d Fourier transform magnitude of k³-weighted in situ Cu K-edge and Fe K-edge EXAFS spectra, respectively. g CO-TPD profiles of Fe1, Cu4, and CuFe samples. h Long-chain alcohols space time yield as a function of Fe5C2 int/(Fe5C2 int + Fe5C2 iso). Fe5C2 int: interfacial Fe5C2; Fe5C2 iso: isolated Fe5C2. The error bars are between 0.002 and 0.003.
reaction (above 600 °C), two desorption peaks at 440 °C and 490 °C (for CuF\textsubscript{2}, CuF\textsubscript{2}Fe, CuF\textsubscript{2}Fe\textsubscript{2}, and CuF\textsubscript{2}Fe\textsubscript{3}) could be attributed to CO desorption from iron carbide\textsuperscript{1,3,52}. With Fe\textsubscript{1} as a reference, these two desorption peaks (440 °C and 490 °C) are attributed to interfacial Fe\textsubscript{5}C\textsubscript{2} (Fe\textsubscript{5}C\textsubscript{2}int) and isolated Fe\textsubscript{5}C\textsubscript{2} (Fe\textsubscript{5}C\textsubscript{2iso}) species, respectively. Clearly, CuF\textsubscript{2}Fe\textsubscript{1} gives the largest integral peak area, indicating the most abundant total Fe\textsubscript{5}C\textsubscript{2} sites than other samples. We fitted and deconvoluted the two peaks to roughly estimate the ratio of Fe\textsubscript{5}C\textsubscript{2}int/(Fe\textsubscript{5}C\textsubscript{2}iso+Fe\textsubscript{5}C\textsubscript{2}int) for these four CuF\textsubscript{2}Fe\textsubscript{i}, and the results showed a volcano correlation between the LA yield and the relative concentration of interfacial Fe\textsubscript{5}C\textsubscript{2} (Fig. 4h). 

CuF\textsubscript{1}Fe\textsubscript{1} catalyst with a moderate Fe\textsubscript{5}C\textsubscript{2}int ratio possesses the highest concentration of Fe\textsubscript{5}C\textsubscript{2}–Cu interface sites (Fe\textsubscript{5}C\textsubscript{2}int), accounting for the largest LA yield (0.101 g g\textsubscript{cat}\textsuperscript{-1} h\textsuperscript{-1}). This demonstrates that the Fe\textsubscript{5}C\textsubscript{2}–Cu interfacial sites act as active centers toward LA production.

It is well-known that CO does not dissociate over Cu; while Fe\textsubscript{2}C (or iron carbide in general) is beneficial for CO dissociation and subsequent C–C bond propagation\textsuperscript{25-27,47,53}. The unique interfacial structure of ultrasmall Fe\textsubscript{5}C\textsubscript{2} clusters over Cu particles has conferred the CuF\textsubscript{2}Fe\textsubscript{1} catalyst a suitable construct for the production of long-chain alcohols at syngas pressure as low as 1 MPa. De Jong et al. reported the size effect in supported iron carbides (2–7 nm) for Fischer–Tropsch reaction, in which a smaller particle size improved the coverage of CH\textsubscript{x} species (the monomer of carbon chain growth)\textsuperscript{54,55}. In this work, long-chain alcohols synthesis at 1 MPa was achieved, which was described to the unique structure of CuF\textsubscript{1}Fe\textsubscript{1} catalyst. The Fe\textsubscript{5}C\textsubscript{2} clusters, with an ultrasmall size (normally below 2 nm) on the surface of Cu nanoparticles, provide active sites for CO activation/dissociation and the resulting C–C bond propagation, which maintains the high activity of CuF\textsubscript{1}Fe\textsubscript{1}. As the reaction pressure decreases from 3 MPa to 1 MPa, hydrogen activation on catalyst surface is weakened (Supplementary Fig. 4), syngas with a flow rate of 40 mL min\textsuperscript{-1} decreases from 3 MPa to 1 MPa. This is also verified by the a–ASF chain-lengthening probabilities analysis: the \textalpha– value for alcohols (0.72) at 1 MPa exceeds that for hydrocarbons (0.70), indicating the rate of CO insertion is larger than that of hydrocarbons chain termination (Supplementary Fig. 4).

Therefore, a precise control over double-active-site in CuF\textsubscript{1}Fe\textsubscript{1} that of hydrocarbons chain termination (Supplementary Fig. 4). Clearly, CuF\textsubscript{1}Fe\textsubscript{1} gives the largest integral peak area, attributed to CO desorption from iron carbide\textsuperscript{51,52}. With Fe\textsubscript{1} as a contrast, the CO activation is promoted since CO molecule is reduced in general activation process.

Catalytic activation. The catalytic evaluation was carried out in a 10-mm fixed-bed stainless-steel reactor. In total, 1.0 g of MMO precursor was loaded on the catalyst bed, and the remaining volume of the reactor tube was filled with quartz beads of 20–40 mesh. Before reaction, the catalyst was activated in situ as mentioned above with a flow rate of 40 mL min\textsuperscript{-1}. After the reactor was cooled to room temperature, syngas with a flow rate of 40 mL min\textsuperscript{-1} (27% CO+55% H\textsubscript{2}+18% N\textsubscript{2}) was introduced to purge the reaction line and reach the required pressure with nitrogen as an internal standard gas. The reaction was conducted at 260 °C. The outlet gas components (CO, H\textsubscript{2}, CH\textsubscript{4}, CO\textsubscript{2}, and N\textsubscript{2}) after passing through a hot trap (180 °C) and a cold trap (5 °C) were determined using an online GC-2014C Shimadzu gas chromatograph with TCD detector (TDX-1 column) and FID detector (AlO\textsubscript{x} packed column) using He as carrier gas. The liquid products were collected from the hot trap and cold trap, followed by determination offline with FID detector (RTX-5). 1,4-dioxane was used as internal standard for the aqueous products, and ethyl cyclohexane was used as an internal standard after extraction by cyclohexane.

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from the corresponding author upon request.

The typical energy of the storage ring was 2.5 GeV with a maximum current beamline of at Beijing Synchrotron Radiation Facility (BSRF) under transmission mode. The catalyst was exposed to CO or H2 for 120 min in room temperature. The catalyst was switched to He exposure until the baseline of the CO or H2 signal leveled off. 

Hydrogen temperature-programmed reduction (H2-TPR) was measured on a ThermoFisher Grand Thermal Analyzer. Elemental analysis for Cu and Fe was performed using a Shimadzu analyzer.

Data availability

The data underlying this study are available from the corresponding author upon request.

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Author contributions

Y.W.L., M.W., and D.M. designed the experiments. Y.W.L. conducted material synthesis and carried out the catalytic performance test. Y.W.L. and M.P. conducted the X-ray absorption fine structure spectroscopy measurements and analyzed the data. X.L. and B.S.Z. contributed to the scanning transmission electron microscopy. W.G., J.B.Z., J.L.S., and Y.X. performed some of the experiments. S.H. contributed to the aberration-corrected high-angle annular dark-field scanning transmission electron microscopy. X.W.L. conducted the Mössbauer spectrum measurements. This paper was primarily written by Y.W.L. All authors contributed to discussions. M.W., B.S.Z., and D.M. conceived the research.

Competing interests

The authors declare no competing interests.

Additional information

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