

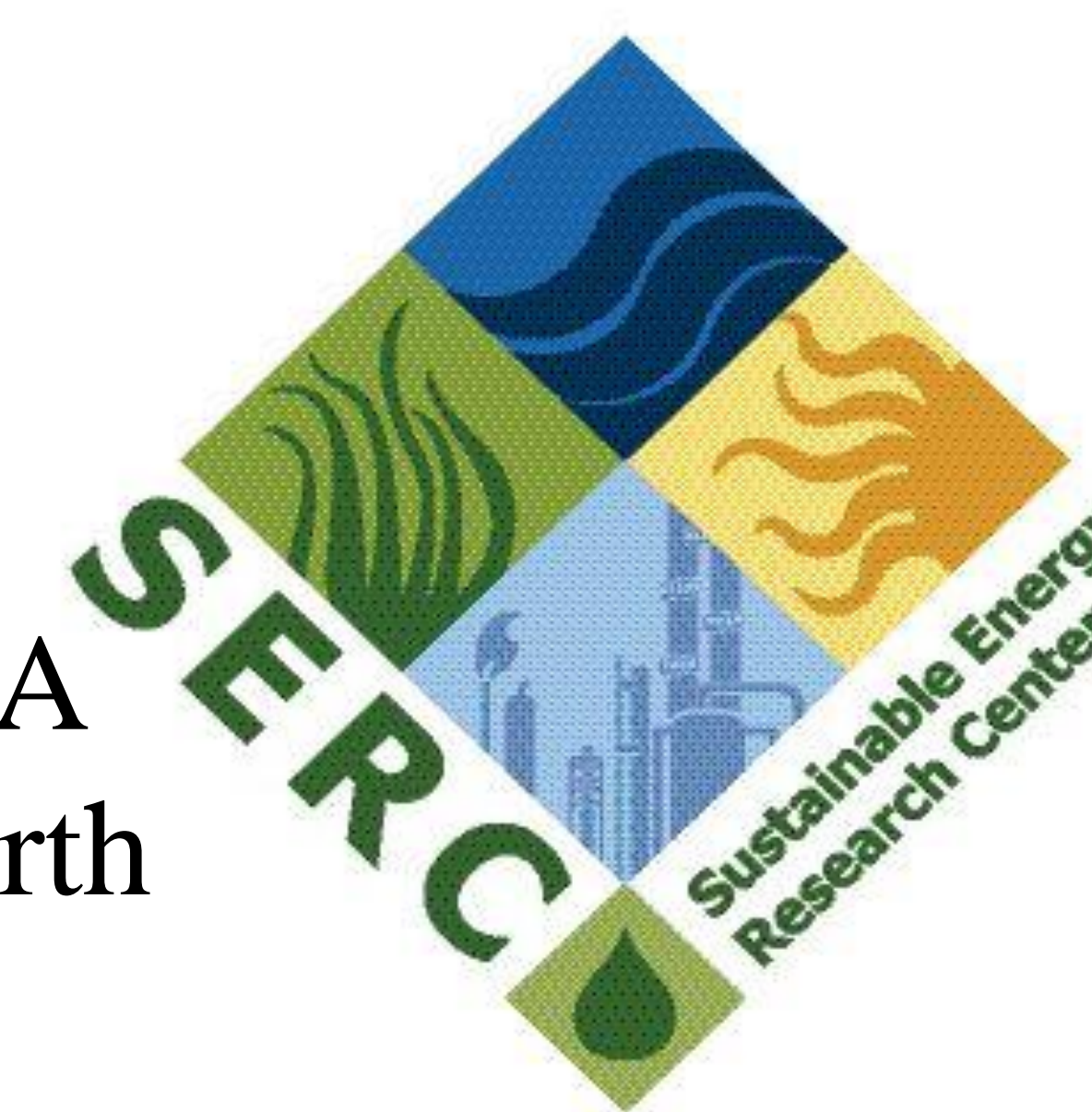
Higher Alcohols Synthesis from Syngas over Three-dimensionally Ordered Macroporous Cu-Fe Bimetallic Catalyst

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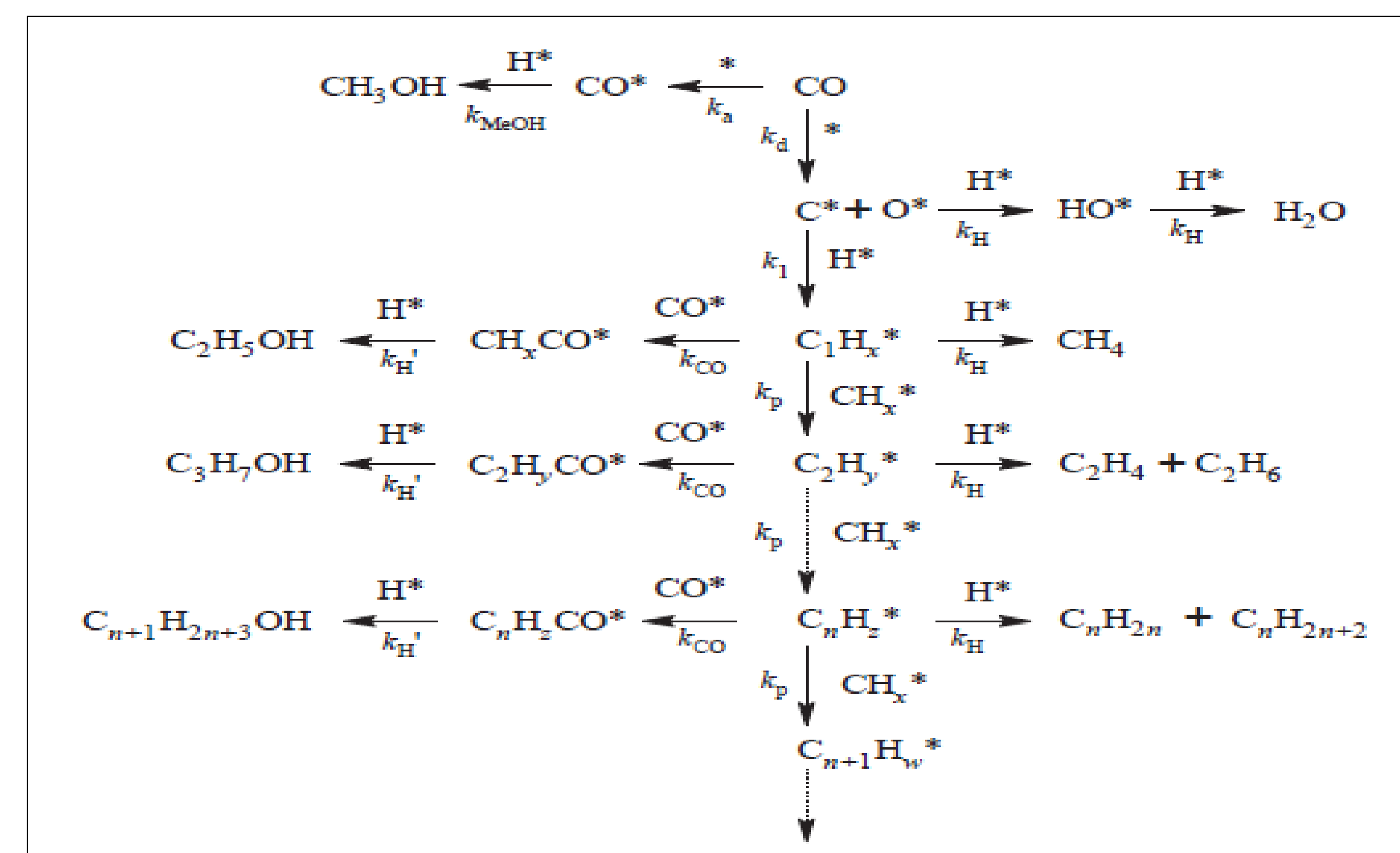
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Introduction

Higher alcohols (C₂₊OH), commonly referred to alcohols higher than methanol, has drawn considerable interest as value-added chemicals, oxygenates fuels or fuel additives. Adding higher alcohols to fossil oil benefits the fuel to combust more completely because of presence of oxygen, which increases the combustion efficiency and reduces air pollution. One promising method of higher alcohols production, is catalytic conversion of mixtures of carbon monoxide and hydrogen (syngas) derived from coal, biomass, natural gas, or shale gas. Although rhodium-based catalysts offer high selectivity (C₂₊OH), their prohibitive cost has urged research on comparable and less expensive copper-based alternatives, mainly modified Fischer-Tropsch (FT) catalysts, such as Cu-Co and Cu-Fe based catalysts. Compared with Cu-Co based catalysts, Cu-Fe based catalysts exhibit higher intrinsic activity and selectivity.

Higher alcohols synthesis (HAS) via modified FT catalysts shares some common reactions with methanol synthesis and FT synthesis (FTS). Methanol synthesis only requires oxygenation, in which an associative C-O bond introduces oxygen into carbon chain. FTS only requires chain propagation, which needs C-O breaking and then hydrogenation into alkenes and alkanes. However, HAS requires a dual site, involving both oxygenation and chain propagation.



To date, Cu active site for methanol synthesis and Fe active site for FTS were deliberately investigated. However, detailed insights into the active Cu-Fe dual site is rare. Thus, it is essentially desirable to unravel the Cu-Fe dual site, in order to gain a fundamental understanding of their intrinsic activity.

Since increasing the dual site surface area and balancing oxygenation and chain propagation reactions on the dual site would be the two key factors to rationally maximize the synergism for HAS, three-dimensionally ordered macroporous (3DOM) catalysts can be one of such promising candidates.

Objective

Design a catalyst to produce higher alcohol with high intrinsic activity and high C₂₊OH selectivity.

Investigate the active sites of the catalyst for higher alcohols synthesis from syngas.

Experimental



Catalyst Characterization

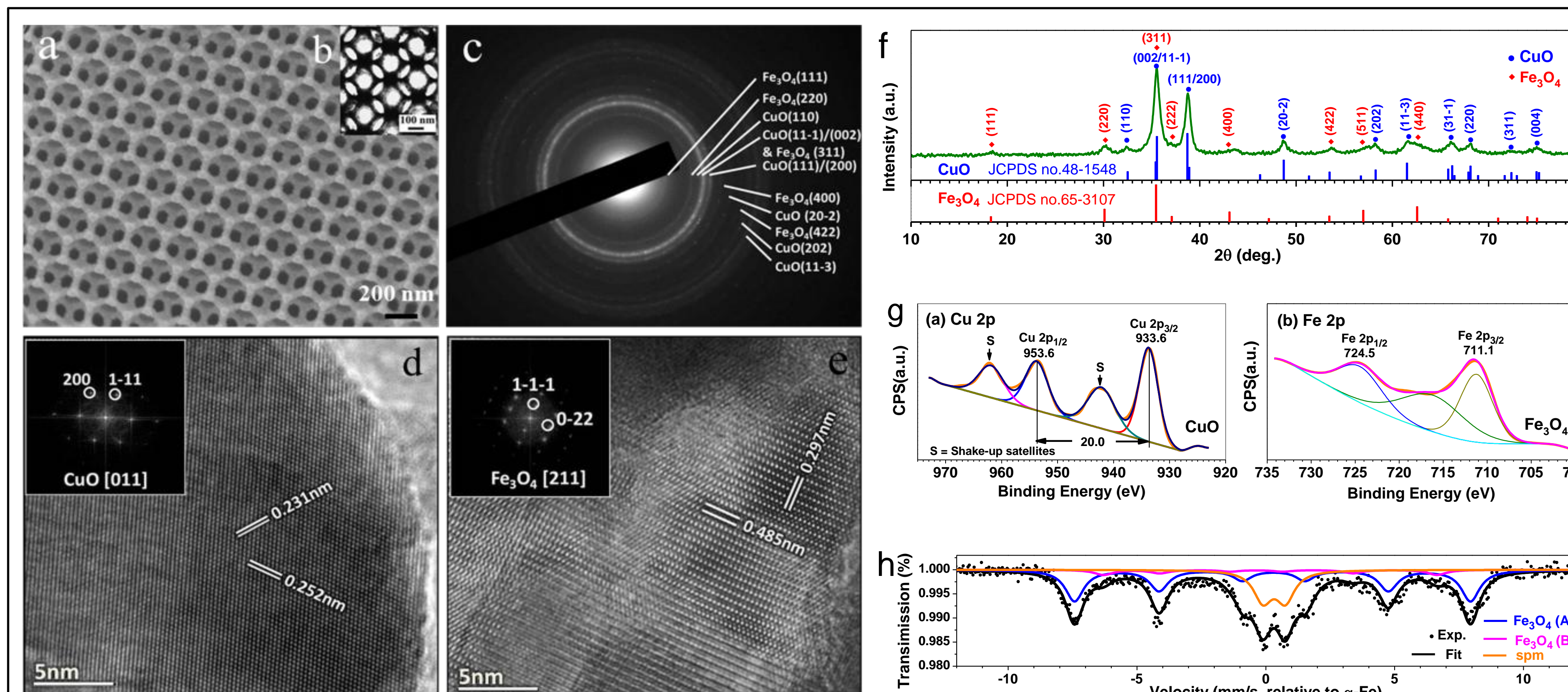


Figure 1. Fresh 3DOM Cu₂Fe₁ catalyst. (a) SEM image and inset (b) TEM image, exhibiting hierarchically macroporous structure containing periodic voids with average diameter 200±10 nm and wall thickness of 50±5 nm. (c) The selected area electron diffraction (SAED) pattern of (b), verifying the catalyst is composed of polycrystalline CuO and Fe₃O₄. (d) HRTEM image of CuO, inset is a Fast Fourier Transform (FFT) image showing CuO aligning along the [011] zone axis; and (e) HRTEM image of Fe₃O₄, inset is a FFT image showing Fe₃O₄ aligning along [211] zone axis. (f) XRD pattern of fresh 3DOM Cu₂Fe₁ catalyst indicates the existence of CuO (JCPDS no. 48-1548) and Fe₃O₄ (JCPDS no. 65-3107). (g) Cu 2p, (h) Fe 2p XPS spectra indicates the existence of CuO and Fe₃O₄ on the surface of the catalyst. (i) Mössbauer spectrum exhibiting two fitted sextets and one fitted doublet reveals the existence of Fe₃O₄ and super-paramagnetic (spm) (Fe³⁺ and/or Fe²⁺) species.

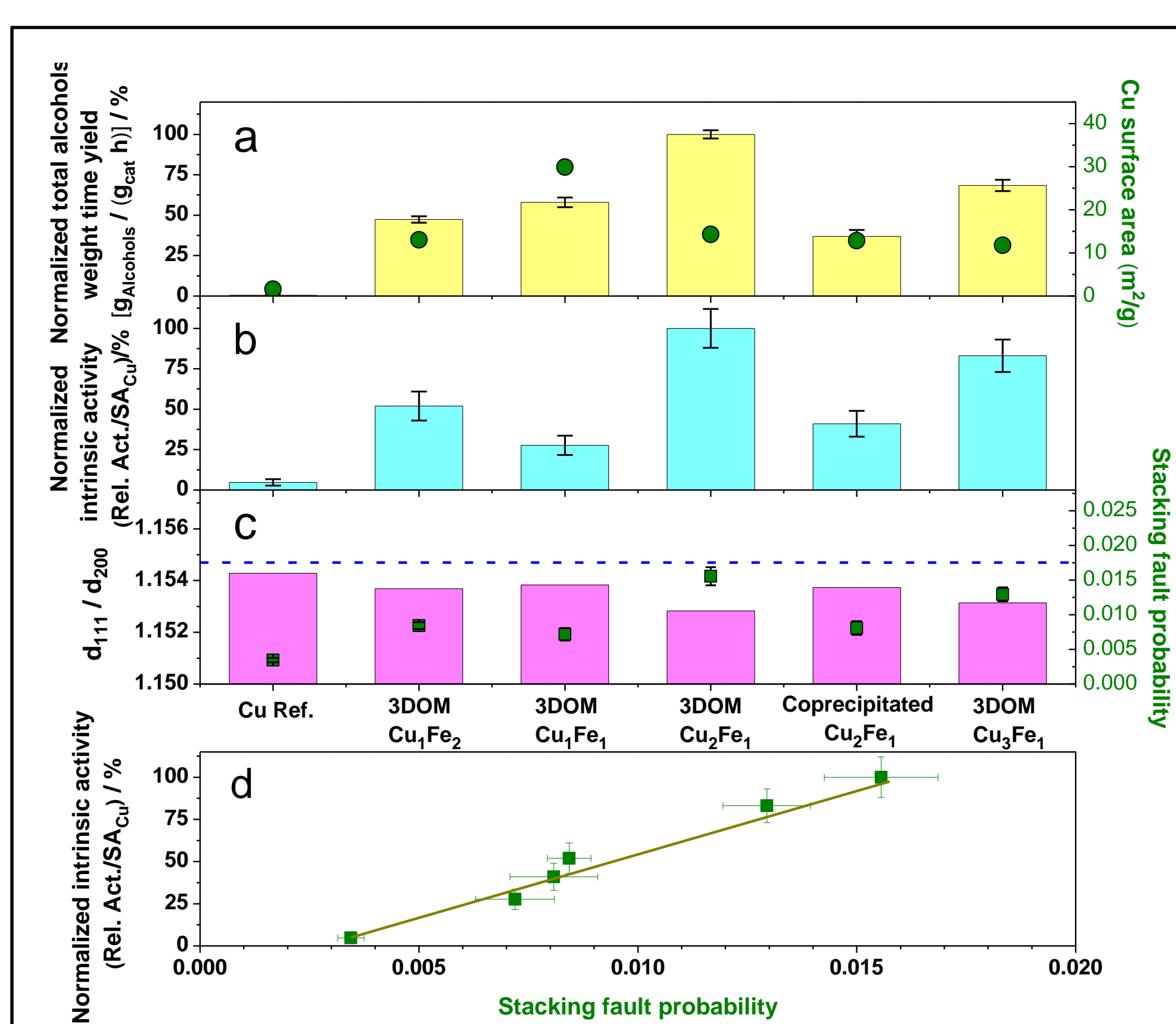


Figure 2. (a) Catalytic activities (total alcohols weight time yield) and Cu surface areas of the catalysts (P = 700 psi, T = 260 °C, GHSV = 2000 h⁻¹, H₂/CO = 1.0, normalized to the most active sample). (b) Intrinsic activities per Cu surface area obtained after dividing by the Cu surface area (normalized to the most active sample). (c) Deviation of d₁₁₁/d₂₀₀ observed in XRD and the resulting Cu stacking fault probabilities. The dashed line refers to the ideal fcc structure (2√3 = 1.1547). (d) Relation of the intrinsic activity of Cu to the stacking fault probability. Error bars indicate uncertainties determined based on replicate measurements (catalytic activity and copper surface area). The error bar of the diffraction peak analysis is according to an estimated uncertainty of 0.1% for the angular peak position.

$$\alpha = 8.3 \times \left[\frac{\sin\theta_{(200)}}{\sin\theta_{(111)}} \right]_{theo} - \left[\frac{\sin\theta_{(200)}}{\sin\theta_{(111)}} \right]_{meas}$$

$$= 8.3 \times \left[\frac{2}{\sqrt{3}} - \left[\frac{\sin\theta_{(200)}}{\sin\theta_{(111)}} \right]_{meas} \right] = 8.3 \times \left[\frac{2}{\sqrt{3}} - \left(\frac{d_{(111)}}{d_{(200)}} \right)_{meas} \right]$$

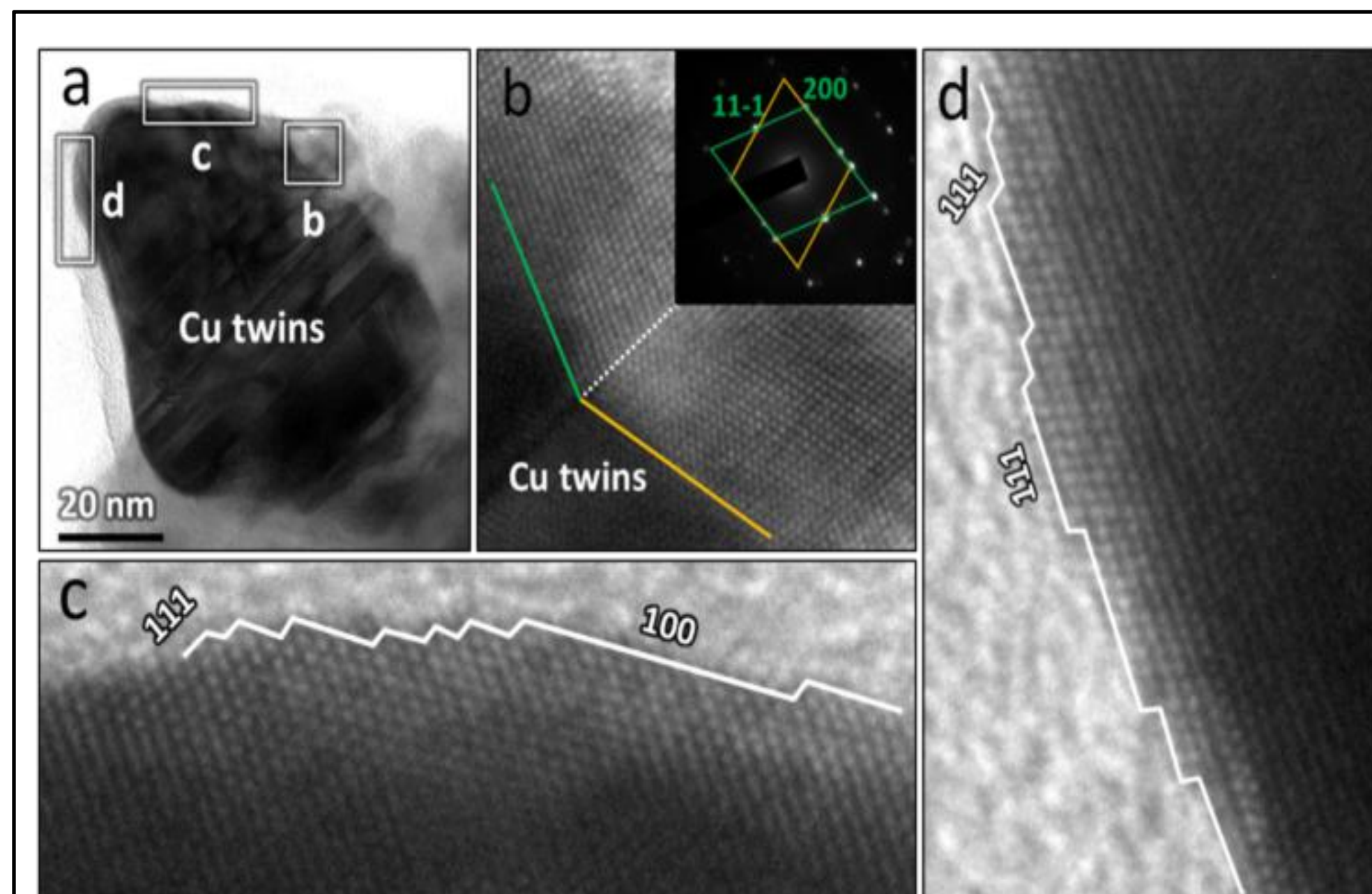


Figure 3. 3DOM Cu₂Fe₁ catalyst after reduction via syngas (H₂/CO=1). (a) HRTEM image shows Cu nanoparticle involving an abundance of twin boundaries (relative dark line). (b) is a close-up of the marked area in (a) representing characteristic Cu twins, inset shows two sets of spot diffraction patterns are highlighted in green and orange colors, corresponding to two sides of twin plane. (c) and (d) are close-ups of the marked area in (a) indicating that atomic Cu steps are formed during transitions between (111) and (100) planes or between (111) planes. These steps will serve as high-activity oxygenation sites. In addition, large amount of twin boundaries and stacking fault would inevitably induce more steps when they terminate at the surface. According to Behrens et al., the presence of steps at the Cu surface, stabilized by stacking faults or twin boundaries terminating at the surface, is one of the reasons for generating high activity for alcohol synthesis.

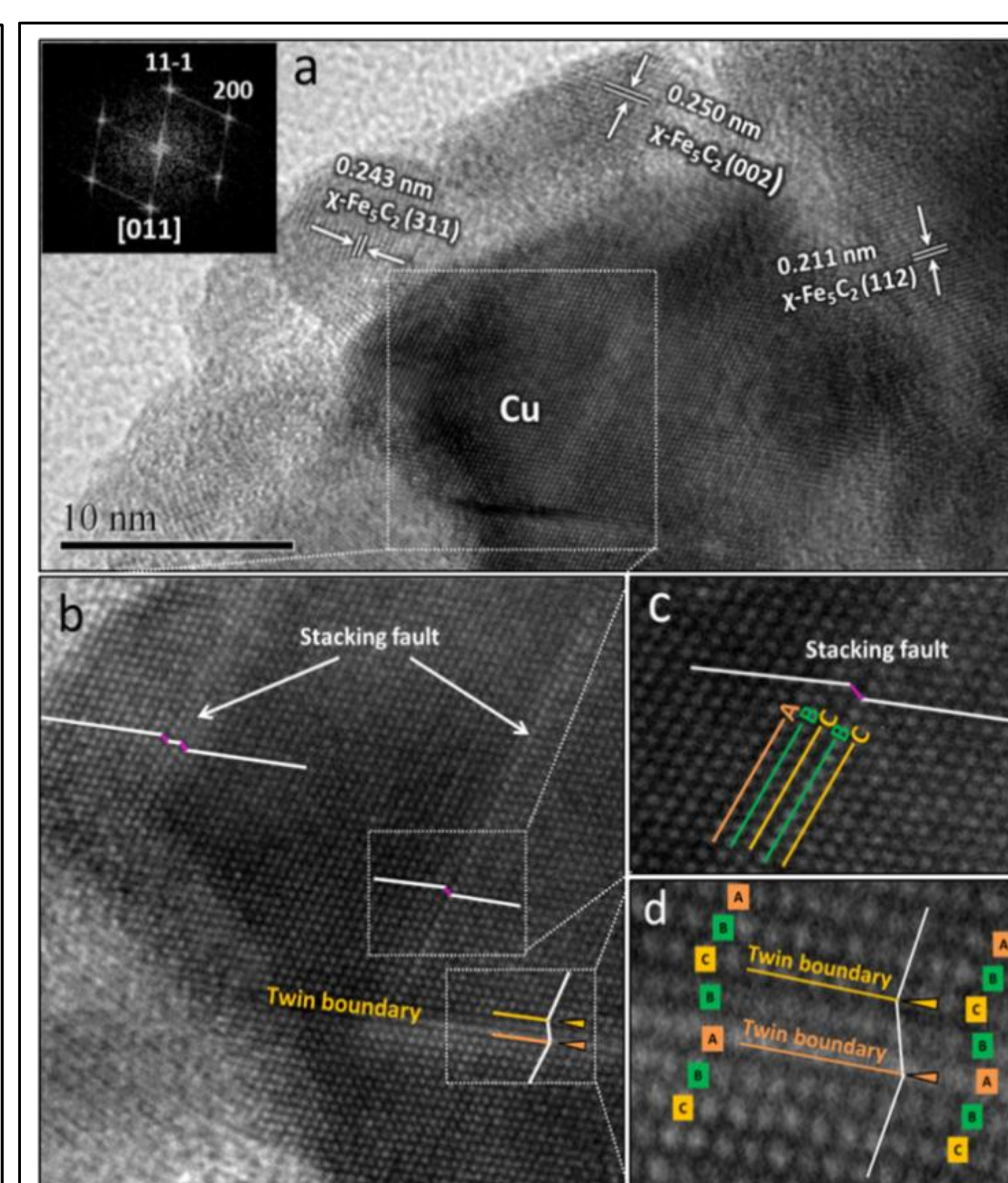


Figure 4. 3DOM Cu₂Fe₁ catalyst after reduction via syngas (H₂/CO=1). (a) HRTEM image, Cu particle containing stacking fault and twin boundaries is surrounded by several Hägg carbide (χ-Fe₅C₂), inset is FFT of Cu [011] zone axis. (b) is a close-up of the dashed marked area in (a). (c) and (d) are close-ups of the dashed line marked area in (b) showing stacking fault and twin boundary, respectively. (e) XRD pattern (Rietveld fit). The characteristic under-estimation of the intensity near maximum of the 200 peak at ca. 50.4° 2θ can be explained with the presence of twin boundaries and stacking faults leading to a broadening of this reflection. (f) Cu 2p XPS and Cu (LMM) Auger spectra, which indicates the existence of Cu⁰ phase; Fe 2p XPS spectrum suggests the existence of χ-Fe₅C₂. (g) The fitted Mössbauer spectrum with three sextets further confirms the existence of χ-Fe₅C₂ phase.

Results and Discussion

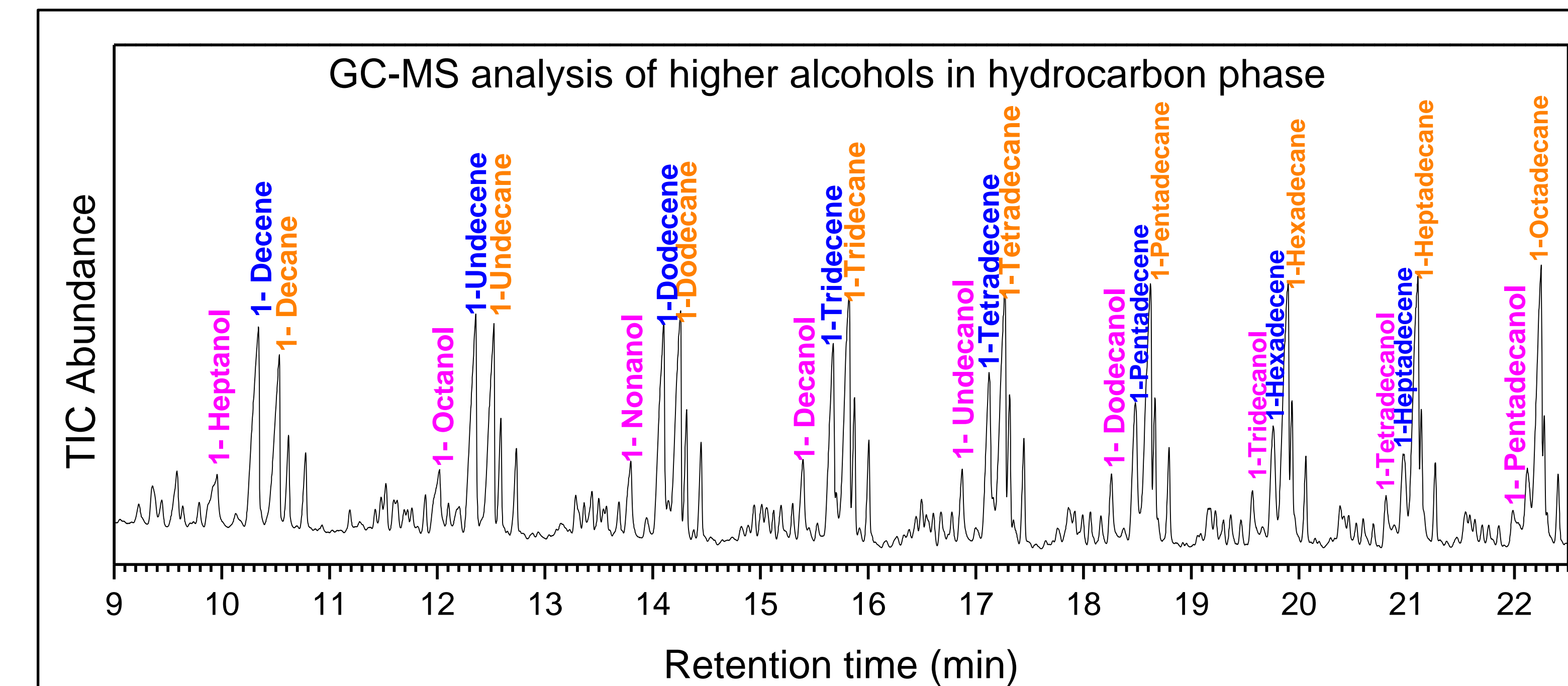
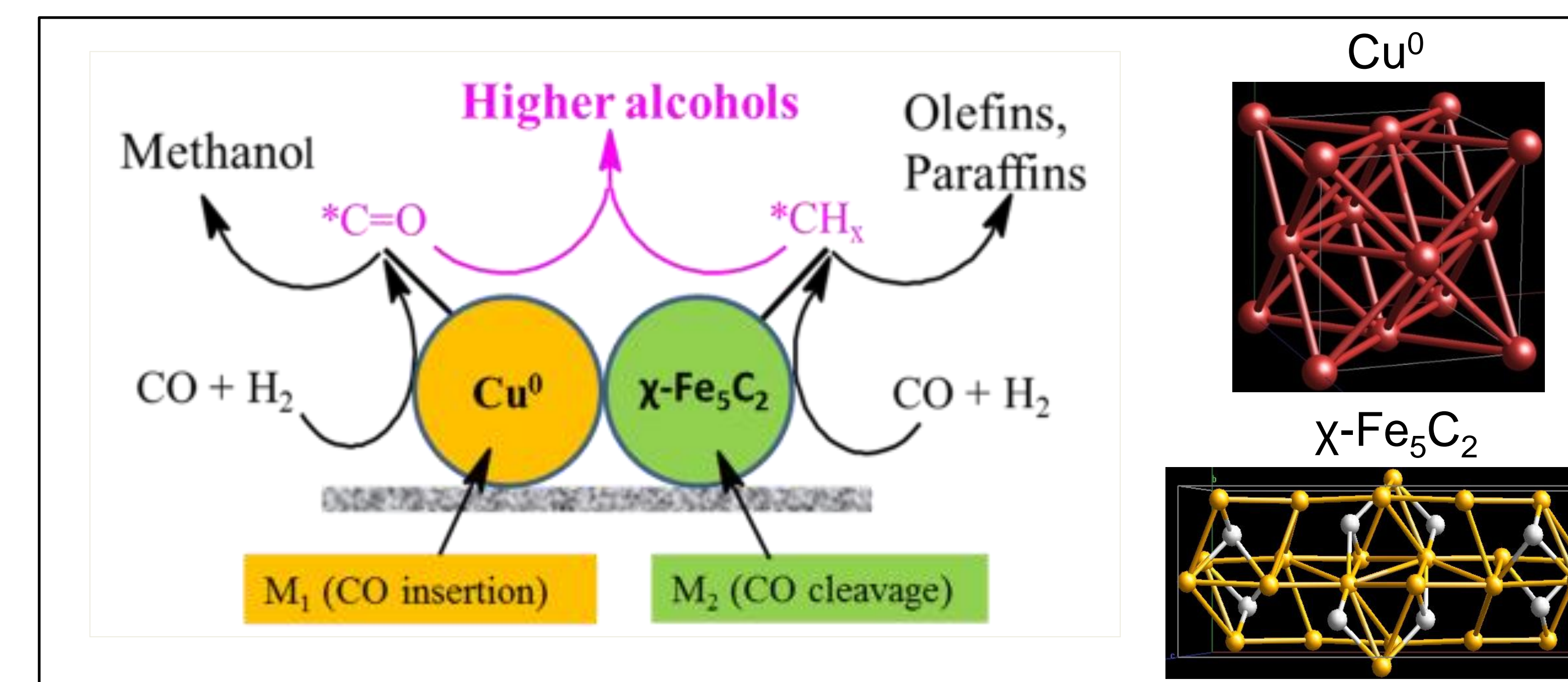


Table 1. Physicochemical Properties and Catalytic Performance^a

| entry | Fresh catalyst (by molar) | S _{BET} (m ² g ⁻¹) ^c | V _{total} (cm ³ g ⁻¹) ^d | d _{meso} (nm) ^e | d _{mic} (nm) ^e | CO Conv. (%) ^f | STY (g mL ⁻¹ (cat.) h ⁻¹) ^g | | Selectivity (%) | | Alcohol (wt.%) | | |
|-------|--------------------------------------------------|-----------------------------------------------------------------|--------------------------------------------------------------------|-------------------------------------|------------------------------------|---------------------------|---------------------------------------------------------------|-----------------|------------------|-----------------|-----------------|--------------------|--------------------|
| | | | | | | | ROH ^h | HC ⁱ | ROH ^h | HC ⁱ | CO ₂ | C ₂ +OH | C ₆ +OH |
| 1 | 3DOM Cu ₂ Fe ₁ | 37.0 | 0.088 | 9.5 | 14.6 | 31.2 | 0.09 | 0.15 | 10.5 | 67.2 | 22.3 | 55.1 | 19.8 |
| 2 | 3DOM Cu ₂ Fe ₁ | 27.7 | 0.076 | 10.9 | 14.5 | 44.3 | 0.11 | 0.13 | 19.8 | 59.8 | 20.4 | 60.3 | 31.6 |
| 3 | 3DOM Cu ₂ Fe ₁ | 43.3 | 0.089 | 8.2 | 14.3 | 58.4 | 0.19 | 0.26 | 31.3 | 57.2 | 11.5 | 83.4 | 45.7 |
| 4 | 3DOM Cu ₂ Fe ₁ | 28.5 | 0.082 | 11.5 | 16.5 | 38.9 | 0.13 | 0.18 | 25.8 | 57.7 | 16.5 | 75.8 | 34.3 |
| 5 | CPT ^b Cu ₂ Fe ₁ | 10.7 | 0.063 | 23.4 | 18.9 | 27.5 | 0.07 | 0.10 | 22.9 | 56.6 | 20.5 | 44.3 | 7.8 |

^aReaction conditions: P = 700 psi, T = 260 °C, GHSV = 2000 h⁻¹, n(H₂)/n(CO) = 1.0. ^bCPT: Coprecipitated. ^cBET specific surface areas evaluated in P/P₀ from 0.05 to 0.9, ±2(m² g⁻¹). ^dTotal pore volumes estimated based on the volume adsorbed at P/P₀ of 0.989, ±0.005(cm³g⁻¹). ^ePore sizes derived from the adsorption branches of the isotherms by using the BJH method, ±0.5nm. ^fAverage crystallite size estimated by the Scherrer equation from XRD pattern, ±0.3nm. ^gCO conversion rate (mol%) = $\frac{CO_{in}-CO_{out}}{CO_{in}} \times 100, \pm 3\%$. ^hSTY (g g⁻¹(cat.) h⁻¹) = $\frac{\text{Weight of product produced (g)}}{\text{Weight of catalyst (g)} \times (\text{h})}$. ⁱROH for alcohols and HC for hydrocarbons.



Conclusions

The self-supported 3DOM Cu-Fe catalysts were applied in higher alcohols synthesis for the first time, having high intrinsic activity and higher alcohols (C₂+OH) selectivity (up to ca. 83% of total alcohols). The unique structure not only eliminates the need for frame support from the third party materials, but also prevents the agglomeration and segregation of both active components to the great extent. The homogeneous distribution of defective Cu and Hägg (χ-Fe₅C₂) nanoparticles help to provide abundant dual sites, resulting in a synergistic effect between Cu⁰ oxygenation site and χ-Fe₅C₂ chain propagation site for higher alcohols synthesis. This finding paves the way towards the rational design of practically relevant dual site catalysts with enhanced intrinsic activity and functionality.

Acknowledgements

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