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ACS Catalysis

Elucidating the Copper–Hägg Iron Carbide Synergistic Interactions for Selective CO Hydrogenation to Higher Alcohols

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ABSTRACT: C0 hydrogenation to higher alcohols (C_2 +OH) provides a promising route to convert coal, natural gas, shale gas, and biomass feedstocks into value-added chemicals and transportation fuels. However, the development of nonprecious metal catalysts with satisfactory activity and well-defined selectivity towards C_2 +OH remains challenging and impedes the commercialization of this process. Here we show that the synergistic geometric and electronic interactions dictate the activity of $Cu^0-\chi$ -Fe₅C₂ binary catalysts for selective C0 hydrogenation to C_2 +OH, outperforming silica-supported precious Rhbased catalysts, by using a combination of experimental evidence from bulk, surface-sensitive, and imaging techniques collected on real and high-performance Cu-Fe binary catalytic systems coupled with density functional theory calculations. The closer the *d*-band center to the Fermi level of $Cu^0-\chi$ -Fe₅C₂(510) surface than those of χ -Fe₅C₂(510) and Rh(111) surface, and the electron-rich interface of $Cu^0-\chi$ -Fe₅C₂(510) due to the delocalized electron transfer from Cu⁰ atoms, which facilitate CO activation and CO insertion into alkyl species to C₂-oxygenates at the interface of $Cu^0-\chi$ -Fe₅C₂(510) and thus enhance C_2H_5OH selectivity. Starting from CHCO intermediate, the proposed reaction pathway for CO hydrogenation to C_2H_5OH on $Cu^0-\chi$ -Fe₅C₂(510) is CHCO+(H)→CH₂CO+(H)→CH₃CO+(H)→CH₃CHO+(H)→CH₃CH₂O+(H)→C₂H₅OH. This study may guide the rational design of high-performance binary catalysts made from earth-abundant metals with synergistic interactions for tuning selectivity.

KEYWORDS: CO hydrogenation, higher alcohols, copper, Hägg iron carbide, synergistic effect, reaction mechanism

INTRODUCTION

Binary metal materials have gained a crucial interest as functional materials for several emerging technologies.^{1–} ⁷ As catalysts, they often exhibit electronic and chemical properties that are distinct from those of their parent metals,^{1,2} thereby enabling the development of novel catalysts with enhanced selectivity, activity, and stability through bifunctional,¹ ligand,² geometric,^{2,3} electronic,³ or lattice strain⁴ effect. The synergistic interaction in binary metal catalyst represents an efficient approach towards desirable properties by either the creation of hybrid sites or the concerted action of concomitant functionalities.^{1,5–7} Binary metal catalysts also show promise of replacing precious metal catalysts with equally active and selective catalysts composed of earth-abundant metals.^{3,5,6}

To decrease the dependence on crude oil and adhere to strict global environmental stipulations, the selective conversion of syngas (CO + H₂) into clean fuels and valueadded chemicals is regarded a primary scientific target.8,9 Syngas can be derived from various carbonaceous resources, such as coal, natural gas, shale gas, municipal solid waste, or biomass feedstocks by using gasification or reforming technologies.^{8,9} The synthesis of ethanol and higher alcohols (C₂₊OH) from syngas leaps out as a catalytic route of prominent interest, because these compounds can be used as hydrogen carriers, fuels, fuel additives in gasoline, precursors for major platform chemicals such as olefins, and reagents for manufacturing pharmaceuticals, cosmetics, lubricants, plasticizers, and detergents.^{5-7,10,11} Additionally, the reaction is a prototypical example that involves the synergistic roles between proximate active

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sites with diverse functionality,^{5–7,10,11} as both CO dissociation (direct or H-assisted dissociation) and CO/CHO insertion into CH_x (x = 1-3) species are required to occur simultaneously to form CH_xCO/CH_xCHO (x = 1-3), thereafter undergoing a stepwise hydrogenation to selectively produce C₂₊OH.^{5–7,10,11} In contrast to methanol synthesis based on Cu-based catalyst⁹ or Fischer–Tropsch synthesis (FTS) of hydrocarbons by using Fe- or Co-based catalysts,^{8,12–14} currently the development of heterogeneous catalysts with high selectivity and space-time yield to achieve commercial-scale C₂₊OH production remains a crucial challenge.^{5–} 7,10,11

Rh is the only single metal reported that can selectively produce C2+OH from syngas, however, its prohibitive cost and scarcity make a large-scale heterogeneous process impossible.^{11,15-19} This has urged the search of inexpensive binary catalysts containing earth-abundant metals such as Cu-Fe catalyst,^{11,20,21} because of its high activity and selectivity that is reported comparable to Rh-based catalysts. However, the origin of the synergistic interaction, the nature of the active sites, and the reaction mechanism for CO hydrogenation to C2+OH over Cu-Fe binary catalysts that play a pivotal role in rational development of robust catalysts for industrial application are not fully understood at the fundamental level. This is partly due to the complexity of the CO hydrogenation reaction on Cu-Fe binary catalyst, whose reactivity is affected by many factors such as geometric, electronic, or bifunctional effect.

Here we show that three-dimensionally ordered macroporous (3DOM) Cu-Fe catalysts exhibit higher performance than that of silica-supported Rh-based catalysts for selective CO hydrogenation to C₂₊OH. Cs-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging and electron energy loss spectroscopy (EELS) elemental mapping is employed to study the Cu-Fe binary active sites. In situ surface chemistry studies are tracked with ambient pressure X-ray photoelectron spectroscopy (AP-XPS) to identify the active sites of Cu-Fe catalyst. In situ X-ray absorption spectroscopy is conducted to reveal the bulk structure of Cu-Fe active sites. Additionally, we perform density functional theory (DFT) calculations to explore the origin of the synergistic interactions, unravel the nature of the active sites, and elucidate the underlying reaction mechanism of Cu-Fe catalyst for selective CO hydrogenation to C₂₊OH at a molecular scale.

RESULTS AND DISCUSSION

Synthesis and Characterization. 3DOM Cu-Fe binary catalysts were synthesized by a "glyoxylate route" poly (methyl methacrylate) colloidal crystal template method²¹ as described in the section of methods. 3DOM Cu₂Fe₁ catalyst with hierarchically macroporous structure contains periodic voids with an average diameter of (200 ± 10) nm and a wall thickness of (50 ± 5) nm (Figure S1). X-ray diffraction (XRD) patterns show that fresh catalysts consist of CuO (JCPDS 48-1548) and Fe₃O₄ (JCPDS 65-3107) (Figure S2). XPS at the Cu 2p and Fe 2p core-levels further confirm the existence of CuO and Fe₃O₄ (Figure S3). HRTEM image of fresh 3DOM Cu₂Fe₁ catalyst is shown in Figure S4a. The lattice fringes of 4.87 and 2.32 Å are characteristic interlayer spacing of Fe₃O₄ (111) and CuO (111) planes, respectively. The indexed selected area electron diffraction pattern (Figure S4b) further manifest the existence of CuO and Fe_3O_4 .

Catalytic Performance. 3DOM Cu-Fe catalysts were reduced *in situ* using H₂/CO = 1 at 300 °C for 48 h. The catalytic tests were performed under a condition of T = 260 , P = 700 psig, H₂/CO = 1, GHSV = 2000 h⁻¹, and time-onstream (TOS) of 120 h after achieving steady state. The selectivity of alcohols, hydrocarbons, and CO₂ is presented in Figure 1a. The representative gas chromatographymass spectrometry (GC–MS) analysis of aqueous and liquid organic products from CO hydrogenation over 3DOM Cu₂Fe₁ catalyst are shown in Figure S5. The 1-alcohols and hydrocarbons distribution agree with Anderson-Schulz-Flory (ASF)^{7,8} distribution (Figure S6), and the calculated ASF chain growth probability (α) of 1-alcohols and hydrocarbons are summarized in Tables S1–S2.



Figure 1. 3DOM Cu-Fe catalysts (a) The selectivity of alcohols, hydrocarbons, and CO₂. (b) The formation rate of C₂₊OH (mmol g_{cat} h⁻¹) (scatter), the selectivity to alcohols and C₂₊OH alcohols (column). (c) Time-on-stream (TOS) evolution of CO conversion. 3DOM Cu₂Fe₁ catalyst (d) TOS evolution of product selectivity. (Reaction conditions: T = 260 °C, P = 700 psig, H₂/CO = 1, and GHSV = 2000 h⁻¹).

3DOM Cu catalyst shows poor activity (Figure 1b). 3DOM Fe catalyst displays a total alcohol selectivity of 4.3%, a C₂₊OH selectivity of 1.3%, and a C₂₊OH formation rate of 0.11 mmol $g_{cat}^{-1}h^{-1}$ (Figure 1b). Importantly, 3DOM Cu-Fe catalysts exhibit a higher activity and selectivity towards C₂₊OH (Figure 1b). At a Cu/(Cu+Fe) atomic ratio of 0.67 (3DOM Cu₂Fe₁), the selectivity to alcohols (31.3%) and C₂₊OH (26.1%) is maximum; meanwhile the formation rate of C₂₊OH reaches 5.65 mmol $g_{cat}^{-1}h^{-1}$, ca. one order of magnitude higher than that of 3DOM Fe catalyst (Figure 1a). The CO conversion is 58.4% for 3DOM Cu₂Fe₁ catalyst without deactivation during TOS of 120 h (Figure 1c). The carbon selectivity to CO₂ (11.5%), hydrocarbons (57.2%), alcohols (31.3%), and C₂₊OH (26.1%) for 3DOM Cu₂Fe₁ catalyst for TOS of 120 h is presented in Figure 1d.

In comparison, we prepared a $(5wt.\%)Rh/SiO_2$ catalyst and tested it in the same reaction condition with that of 3DOM Cu₂Fe₁ catalyst. The XRD patterns of the fresh and reduced $(5wt.\%)Rh/SiO_2$ are shown in Figure S7, where Rh species is identified as RhO₂ (JCPDS 21-1315) and Rh (JCPDS 05-0685), respectively. The catalytic performance

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of $(5wt.%)Rh/SiO_2$ catalyst shows a CO conversion of 6.3%, C₂₊OH selectivity of 11.2 %, and C₂₊OH formation rate of 0.63 mmol g_{cat⁻¹}h⁻¹ (Table S3). Thus, the catalytic performance of 3DOM Cu₂Fe₁ shows a CO conversion of 58.4%, C₂₊OH selectivity of 26.1%, and C₂₊OH formation rate of 5.65 mmol g_{cat⁻¹}h⁻¹, which is much higher than that of $(5wt.%)Rh/SiO_2$, and a select of other silica-supported Rhbased catalysts (Table S3) reported in the literatures.¹⁵⁻¹⁸

The catalytic performances of 3DOM Cu-Fe catalysts indicate that the activity and selectivity may attribute to the synergistic interfacial interactions of Cu-Fe binary active sites. To further validate the hypothesis of the synergistic interfacial interactions, we prepared a physical mixture (PM) of 3DOM Fe and 3DOM Cu catalyst, denoted as 3DOM PM-Cu₂Fe₁, and tested it in the same reaction condition with those of 3DOM Cu-Fe catalysts. 3DOM PM-Cu₂Fe₁ catalyst shows a CO conversion of 24.5% (Figure 1c), C_{2+} OH selectivity of 1.1%, and C_{2+} OH formation rate of 0.11 mmol $g_{cat}^{-1}h^{-1}$ (Figure 1b), which is much less active and selective for C_{2+} OH production than that of 3DOM Cu₂Fe₁ catalyst. Furthermore, the calculated intrinsic activity of 3DOM Cu₂Fe₁ catalyst is 6.6×10^{-2} mmol m⁻² h⁻¹ (Table S4), which is one order of magnitude higher than that of 3DOM PM-Cu₂Fe₁ catalyst (2.0×10^{-3} mmol m⁻² h⁻¹).



Figure 2. 3DOM Cu-Fe catalysts after reduction (a) XRD pattern and (b) Mössbauer spectra. 3DOM Cu₂Fe₁ catalyst after reduction (c) HAADF-STEM image and (d–g) EELS mapping of the selected region (green box) showing elemental distribution of C (d), Fe (e), Cu (f), and their overlap (g). Cs-corrected HAADF-STEM images (h) $Cu^0-\chi$ -Fe₅C₂(510) that involves Cu step and twin boundary, inset the fast Fourier transform of the selected region (red dashed box) showing Cu⁰ is aligned along the [110] zone axis. (i) The magnification of white dashed box in (h).

Structural Characterization of the Catalytic Active Sites. XRD and Mössbauer spectroscopy were used to identify the active sites of 3DOM Cu-Fe catalysts after reduction at 300° C using H₂/CO = 1 for 48 h. The long reduction time of 48 h was applied to ensure the complete reduction and carburization of iron oxide in the 3DOM catalysts into iron carbide. XRD pattern of the reduced catalysts (Figure 2a) indicate that CuO is reduced to Cu⁰ (JCPDS 004-0836), and Fe₃O₄ is reduced and carburized into Hägg carbide (χ -Fe₅C₂) (JCPDS 051-0997). Figure 2b shows Mössbauer spectra of reduced catalysts that can be fitted with three sextets and one doublet, representing χ -Fe₅C₂ with different hyperfine parameters.^{8,22} The fitting Mössbauer parameters are summarized in Table S5. Figure 2c shows HAADF-STEM image of reduced 3DOM Cu₂Fe₁ catalyst, and the green box indicates the selected region for EELS elemental mapping. As shown in EELS elemental maps (Figure 2d–g), the catalyst reduction treatment ended finally with Cu species intimate contact with iron carbide species. Cs-corrected HAADF-STEM image (Figure 2h) displays the lattice fringe of 2.05 Å from χ -Fe₅C₂(510) (JCPDS 051-0997) is closely adjacent to Cu⁰ to generate intimate and extensive interface. The inset in Figure 2h is the fast Fourier transform of the selected region (red dashed box), indicating that Cu⁰ is aligned along the [110] zone axis. Cu⁰ involves typical Cu step and twin boundary (Figure 2h). Figure 2i is the magnification of the selected region (white dashed box) in Figure 2h. Because neither Cu nor χ -Fe₅C₂ alone could achieve the high selectivity of C₂₊OH in 3DOM Cu-Fe catalysts (Figure 1), we advocate the formation of the Cu⁰- χ -

Fe₅C₂ binary active sites (Figure 2i) and their synergistic interactions that result in the observed catalytic performance.

In situ Studies of Surface Chemistry Using AP-XPS. To achieve a deep insight into the Cu-Fe binary active sites for CO hydrogenation, we performed *in situ* AP-XPS. During the data acquisition of *in situ* studies, the gaseous reactants remained around catalyst at a certain temperature. The fresh 3DOM Cu₂Fe₁ catalyst was pretreated *in situ* with 1.0 mbar O₂ at 300°C for 3 h to remove any residual carbonaceous surface species (Figure 3). The Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks are accompanied with distinct shakeup satellites at binding energies of 942 and 962 eV after O₂ pretreatment (Figure 3a). These characteristic satellites stem from charge transfer between the transition metal 3d and surrounding ligand oxygen 2p orbitals, and they do not present in Cu₂O and Cu⁰ because of their fully filled 3d orbitals.²³ The Cu 2p_{3/2} peak at binding energy of 933.6 eV (Figure 3a) is thus indicative of CuO.²⁴ The broadening of main Cu LMM peak at 918.0 eV to lower kinetic energies was found during *in situ* reduction up to 100°C (Figure 3b). The drop of shakeup satellite intensity and the shift of Cu 2p_{3/2} peak to lower binding energy indicate the formation of monovalent copper (Cu⁺).²⁴ Upon heating to 150°C, the appearance of Cu LMM peaks at 918.6 and 921.3 eV can be attributed to metallic copper; meanwhile, no shakeup satellite of Cu²⁺ species was detected in Cu 2p spectra.^{24–26}



Figure 3. *In situ* AP-XPS studies of 3DOM Cu₂Fe₁ catalyst surface with O₂ pretreatment at different temperatures in H₂ and CO (H₂/CO=1) at mbar pressure range. (a) Cu 2p, (b) Cu LMM, (c) Fe 2p and (d) C 1s.

After in situ reduction with $H_2/CO = 1$ at 100 and 150°C, there are no measurable carbon species presented on the catalyst surface (Figure 3d). Upon heating to 200°C, the iron oxide after O₂ pretreatment was partially carburized into iron carbide, as indicated by the appearance of a peak at 283.5 eV in C 1s spectra.²⁷ The shift of the binding energy of Fe 2p_{3/2} peak from 710.7 to 707.3 eV (Figure 3c) further corroborates that the formed iron carbide is x-Fe₅C₂,^{14,28} which is consitent with Mössbauer spectra analysis (Figure 2b). Upon heating to 250°C, the carbide peak is associated with a shoulder at 284.6 eV (Figure 3d), which is assigned to the occurrence of generic non-oxygenated surface carbon species (C_{surf}).²⁷ The evolution of Cu/(Cu+Fe) atomic ratio under various reaction conditions (Figure 3) is close to nominal composition of 0.67 (Figure S8), indicating no preferential surface enrichment of Cu or Fe species upon in situ reduction. We also performed in situ AP-XPS studies for 3DOM Cu2Fe1 catalyst without O2 pretreatment (Figure S9): (I) in UHV, (II) in $H_2/CO = 1$ at RT, (III) in $H_2/CO = 1$ at 100–500°C, and (IV) cooling to 280, 260, and 220°C in $H_2/CO = 1$. The copper phase remains metallic state (Figure S9a-b) during catalysis at 280, 260, and 220°C. The iron phase keeps x-Fe₅C₂ state (Figure S9c), albeit the existence of residual carbonaceous surface species (at 284.5 eV) before catalysis renders the iron carbide peak at 283.5 eV of C 1s spectra (Figure S9d) indiscernible. Cu^0 and χ -Fe₅C₂ are thus elucidated as the binary active sites for CO hydrogenation. In situ X-ray Absorption Spectroscopy Studies. The revealing of Cu⁰ and χ -Fe₅C₂ binary active sites from *in situ* AP-XPS are corroborated by in situ X-ray Absorption Near

Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) studies for 3DOM Cu₂Fe₁ catalyst at Cu and Fe K-edge with H₂/CO = 1 (Figure 4). The fitted $k^{3}\chi(k)$ (k-space plot), Fourier transforms of $[k^{3}\chi(k)]$ (Rspace plot), and Re[$\chi(q)$] (Å⁻³) (q-space plot) spectra for the Cu K-edge and Fe K-edge signals of 3DOM Cu₂Fe₁ catalyst at RT and 300°C are illustrated in Figures S10–S11, respectively, and the fitted parameters are summarized in Table S6.

The XANES spectra of 3DOM Cu₂Fe₁ catalyst (CO+H₂@RT) at Cu K-edge (8979 eV) (Figure 4a) illustrate that there are two characteristic peaks for CuO. The first one at 8978 eV originated from the weak quadrupoleallowed Cu 1s-to-3d transition.²⁹⁻³¹ The second one, a shoulder peak at 8986 eV, could be ascribed from the dipole-allowed 1s-to-4p "shakedown" transition because of the interaction between the metal and ligand.^{29,31} The fitting FT[$k^3\chi(k)$] of Cu K-edge EXAFS (CO+H₂@RT) is presented in Figure S10c. The peak at 1.94 Å for CuO is assigned to the first Cu-O coordination shell. Two peaks determined at 2.90 Å and 3.45 Å are associated with the Cu-Cu coordination shells.^{32,33} Apart from these peaks, a broad peak observed at 5.74 Å is attributed to the third Cu-Cu coordination shell. The fitted scattering paths at 1.942 Å (Cu-O bond) and 2.849 Å (Cu²⁺-Cu²⁺ bond) (CO+H₂@RT) are characteristic of CuO (Table S6).32,33 After in situ reduction (\geq 250°C), the XANES spectra are similar with Cu foil spectrum (Figure 4a). The EXAFS spectra (CO+H₂≥250°C) were fitted with theoretical model of Cu.34,35 The fitting $FT[k^3\chi(k)]$ of Cu K-edge EXAFS spectra (CO+H₂@300°C) is presented in Figure S10d. The fitted scattering path at

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59 60 2.543 Å (Table S6) can be assigned to the Cu–Cu bond of metallic copper.^{34,35}

The XANES spectrum (CO+H₂@RT) at Fe K-edge (7112 eV) are within the range expected for Fe₃O₄ (Figure 4c). Fe₃O₄ has the cubic inverse spinel structure with Fe²⁺ cations in octahedral sites and Fe³⁺ cations in both octahedral and tetrahedral sites, surrounded by oxygen ions.³⁶ Both octahedral and tetrahedral iron atoms contribute to R-space plot. A theoretical model of Fe₃O₄ with five scattering paths was used to fit the EXAFS spectra (CO+H₂ \leq 250°C). There are two main features for Fe₃O₄ in R-space plot (Figure 4d), a peak centered at 1.5 Å consisting of nearest-neighbor oxygen coordination shell contributions (Fe_{tet}–O and Fe_{oct}–O), and a second peak with maximum intensity at

2.6 Å and a broad shoulder at 3.1 Å.^{36,37} The second peak consists of several Fe–Fe (Fe_{tet}–Fe_{tet}, Fe_{tet}–Fe_{oct}, and Fe_{oct}–Fe_{oct}) and Fe–O (Fe_{tet}–O and Fe_{oct}–O) scattering contributions.^{36,37} The fitted scattering path at 1.932 Å (Fe_{oct}–O bond) and 3.319 Å (Fe_{tet}–Fe_{tet} bond) (Figure S11c, Table S6) are characteristic of Fe₃O₄ for 3DOM Cu₂Fe₁ catalyst (CO+H₂@RT).^{36,37} After *in situ* reduction (\geq 300°C), the XANES spectra are similar with χ -Fe₅C₂ spectrum (Figure 4c). The EXAFS spectra (CO+H₂ \geq 300°C) were fitted with theoretical model of χ -Fe₅C₂.³⁸ Taking 3DOM Cu₂Fe₁ catalyst (CO+H₂@300°C) as an example (Figure S11d), the fitted scattering paths at 1.645 Å (Fe–C bond) and 2.578 Å (Fe–Fe bond) (Table S6) attribute to χ -Fe₅C₂.^{38–40}



Figure 4. In situ X-ray absorption spectroscopy studies for 3DOM Cu_2Fe_1 catalyst at different temperatures with $H_2/CO = 1$. (a) Cu K-edge XANES, (b) Fourier transform magnitude of k^3 -weighted of Cu K-edge EXAFS spectra, (c) Fe K-edge XANES, (d) Fourier transform magnitude of k^3 -weighted of Fe K-edge EXAFS spectra.

The Cu⁰-x-Fe₅C₂ Synergistic Interactions. Linear 1alcohols were mainly produced on $Cu^0-\chi$ -Fe₅C₂ binary catalysts based on the GC-MS results (Figure S5). We envisioned the formation of higher alcohols via the hydroformylation^{6,7} of the olefin intermediates from FTS reaction, because otherwise, it would produce branch-alcohols. Additionally, the alcohol and hydrocarbon distributions on $Cu^0-\chi$ -Fe₅C₂ catalysts (Figure S6) are found similar and follow ASF distributions.^{7,8} The FTS reaction on χ -Fe₅C₂ catalysts follow ASF distribution as well (Figure S6). The similar ASF distribution of 1-alcohols and hydrocarbons found on $Cu^0-\chi$ -Fe₅C₂ binary catalysts implies that the chain propagation may occur primarily on x-Fe₅C₂, providing the active site for which CO dissociates and hydrogenates to alkyl species, thereby initiating the chain growth through $CH_x + CH_x$ (x = 1–3) coupling.¹¹ The χ -Fe₅C₂ catalyst was well reported for its selective synthesis of linear hydrocarbons in FTS reaction,^{8,12,14,22} which corroborates the present finding of linear 1-alcohols formed on Cu⁰-x-Fe₅C₂ catalysts. Thus, the essence of Cu⁰ in Cu⁰- χ -Fe₅C₂ catalysts could be rationalized by providing the active sites for CO associative adsorption, in combination with the linear hydrocarbon intermediates formed on the χ -Fe₅C₂ part at the interface of $Cu^0-\chi$ -Fe₅C₂ to generate linear oxygenates, which are hydrogenated to selectively produce linear 1-alcohols.¹¹ To shed further light on the Cu⁰- χ -Fe₅C₂ synergistic interactions for selective CO hydrogenation to higher alcohols, we resorted to density functional theory (DFT) calculation on $Cu^0 - \chi - Fe_5C_2(510)$ surface model (Fig-

ure 5) based on the HAADF-STEM result (Figure 2i) in comparison to χ -Fe₅C₂(510) surface model (Figure S12). Reaction Pathway on χ -Fe₅C₂(510). The χ -Fe₅C₂(510) surface morphology and its adsorption sites is illustrated in Figure S12. The most stable adsorption configuration of reactants, products, and possible intermediates involved in CO hydrogenation to C₂-hydrocarbon and C₂-oxygenates on χ -Fe₅C₂(510) are shown in Figure S13, and the corresponding adsorption energy and key geometrical parameters are listed in Table S7. The routes of CO activation, and the formation of CH_x (x = 1–3), CH_3OH , C_2 -hydrocarbons, and C_2 oxygenates on χ -Fe₅C₂(510) are presented in Figures S14– S21. All possible elementary reactions involved in CO hydrogenation to C₂-hydrocarbons and C₂-oxygenates together with activation barriers and reaction energies on χ - $Fe_5C_2(510)$ are listed in Table S8. The reaction pathway for CO hydrogenation on χ -Fe₅C₂(510) is shown in Figure S22.

On χ -Fe₅C₂(510), CO direct dissociation and CO hydrogenation to CHO are more favorable than CO hydrogenation to COH (Figure S14). Meanwhile, CO direct dissociation and CO hydrogenation to CHO are kinetically competitive due to their close activation barriers. C and CHO are thus the major intermediates of CO activation. Starting from the initiate states of C+H, CHO, and CHO+H, C hydrogenation to CH is more favorable than the other pathways (Figure S15). This suggests that C hydrogenation mainly contributes to CH formation, which is kinetically competitive with CH₂O formation. Starting from the initiate states of CH+H, CHO+H, and CH₂O, both CH hydrogenation and CH₂O dissociation with H-assisted significantly contribute to CH₂ formation (Figure S16). Furthermore, CH₂ formation is more favorable than CH₃O or CH₂OH (Figure S16). Starting from the initial states of CH₂+H, CH₂O+H, and CH₃O, CH₂ hydrogenation mainly results in CH₃ formation, which is more favorable than CH₃OH formation (Figure S17). CH is thus the most favorable CH_x (x = 1-3) species on χ -Fe₅C₂(510) (Figure S18). Additionally, CH formation is more favorable than CH₃OH formation, suggesting that χ -Fe₅C₂(510) exhibits higher selectivity to CH species instead of CH₃OH (Figure S18 and Figure S22).

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On x-Fe₅C₂(510), CH prefers coupling to C₂H₂ rather than dissociation to C, hydrogenation to CH₂, or being inserted by CO/CHO to C2-oxygenates (Figure S19). CH2 prefers dissociation to CH rather than hydrogenation to CH₃, coupling to C₂H₄, or being inserted by CO/CHO to C₂oxygenates (Figure S20). CH3 prefers dissociation to CH2 instead of hydrogenation to CH₄, coupling to C₂H₆, or being inserted by CO/CHO to C₂-oxygenates (Figure S21). Once CH₂ and CH₃ are formed on χ -Fe₅C₂(510), both would dissociate to CH, further confirming that CH is the most favorable CH_x (x = 1-3) species. Our calculation results are in excellent agreement with the experimental results14,22 and DFT calculations⁴¹⁻⁴³ that χ -Fe₅C₂ exhibits good catalytic performance for CO dissociation¹² and carbon-chain propagation for Fe-based FTS catalysts. Thus, CH is the most favorable species on χ -Fe₅C₂(510), and χ -Fe₅C₂(510) mainly contributes to the formation of C₂H₂ via CH coupling (Figure S22, Supplementary Movie 1).

The Cu⁰–\chi-Fe₅C₂(510) **Surface Model**. To further elucidate the synergistic interactions of Cu⁰– χ -Fe₅C₂ binary catalyst for selective CO hydrogenation to higher alcohols, we resorted to DFT calculation on a Cu⁰– χ -Fe₅C₂(510) surface model (Figure 5) based on HAADF-STEM result (Figure 2i). We construct a Cu strip adsorbed on a $p(2 \times 1) \chi$ -Fe₅C₂(510) surface to optimize and represent Cu⁰– χ -Fe₅C₂ binary catalyst. The Cu⁰– χ -Fe₅C₂(510) surface morphology and its adsorption sites are also shown in Figure 5.

The Geometric Effect of Cu⁰-x-Fe₅C₂(510). The geometric effect plays a crucial role in catalytic performance, as it associates with the atomic arrangement at the active site.^{2,3,44} The way the active site is configured can exert a significant effect on the binding strength of adsorbates.^{3,44} The calculated geometric results show that only CO prefers adsorption at the interface of $Cu^0 - \chi - Fe_5C_2(510)$, while CH_x (x = 1-3) and H species prefer adsorption at the top Fe sites on Cu⁰-x-Fe₅C₂(510) surface (Figure S23). Moreover, as shown in Table S9, the calculated adsorption energies of CH_x (x = 1-3) and H species decrease and the calculated CO adsorption energy increases on Cu⁰-x-Fe₅C₂(510) in comparison to those on χ -Fe₅C₂(510). Additionally, among all reactions related to $CH_x(x = 1-3)$ (Figures S24–S26), the reactions of their dissociation, hydrogenation, and coupling to C₂-hydrocarbons prefer occurring at the Fe sites on $Cu^0 - \chi$ -Fe₅C₂(510). However, only CO insertion into CH_x (x = 1-3) to C₂-oxygenates occur at the interface of Cu⁰- χ -Fe₅C₂(510) (Figures S24–S26). Thus, χ -Fe₅C₂(510) alone mainly contributes to C₂-hydrocarbons formation, and the geometric effect at the interface of $Cu^0 - \chi - Fe_5C_2(510)$ plays an important role in C₂-oxygenates formation.

On χ -Fe₅C₂(510), it is noteworthy that CHO insertion into CH_x (x = 1-3) to CH_xCHO (x = 1-3) are all more kinet-

ically difficult owing to their higher activation barriers than CO insertion into CH_x (x = 1-3) to CH_xCO (x = 1-3) (Figures S19–S21). Therefore, on $Cu^0-\chi$ -Fe₅C₂(510), we will only consider CO insertion into CH_x (x = 1-3) species to C₂-oxygenates. On Cu⁰- χ -Fe₅C₂(510) surface, CH₃ prefers dissociation to CH₂ (Figure S26). Thus, CH and CH₂ are found to be the most favorable CH_x species on $Cu^0-\gamma$ -Fe₅C₂(510). The adsorbed CO at the interface of Cu⁰- χ -Fe₅C₂(510) inserts into CH_x (x = 1, 2) that adsorbed at the Fe sites of χ -Fe₅C₂(510) surface to C₂-oxygenates (CHCO/CH₂CO) with the activation barriers of 64.8 and 32.5 kJ·mol⁻¹, respectively (Figure 6a). Whereas on χ -Fe₅C₂(510), the activation barriers are 144.5 and 113.3 kJ·mol⁻¹, respectively, which are much higher by 79.7 and 80.8 kJ·mol⁻¹ than those on $Cu^0 - \chi - Fe_5C_2(510)$ (Figure 6a). Additionally, the previous DFT calculation reported by Zhao et al.45 on Rh(111) for CO hydrogenation to C2oxygenates indicated that CO insertion into $CH_x(x = 1, 2)$ had activation barriers of 129.3 and 120.6 kJ·mol⁻¹ (Table S9), respectively, which are much higher by 64.5 and 88.1 kJ·mol⁻¹ than those on Cu⁰– χ -Fe₅C₂(510). Thus, the smaller activation barriers required for CO insertion into $CH_x(x =$ 1, 2) to C₂-oxygenates (CHCO/CH₂CO) suggest that Cu⁰- χ -Fe₅C₂(510) is indeed favorable for higher alcohols formation compared with χ -Fe₅C₂(510) and Rh(111).



Figure 5. The Cu⁰- χ -Fe₅C₂(510) surface model. A Cu strip adsorbed on χ -Fe₅C₂(510) surface and its adsorption sites with top and side view. T1–T4 denote the top Fe site of χ -Fe₅C₂(510) surface, and T₁5–T₁10 denote the top Fe or Cu sites of Fe–Cu interface; B1–B6 and B7–B12 denote the Fe–Fe bridge and Cu–Cu bridge sites, respectively; B₁1–B₁3 denote the Fe–Cu bridge sites of Fe–Cu interface; F1–F4 denote the 3fold Fe sites of χ -Fe₅C₂(510) surface, F5 and F6, F7 denote the 4-fold and 3-fold Cu sites over Cu strip, respectively; F₁1 and F₁2 denote the 3-fold sites of Fe–Cu interface. The interface between Cu⁰ and χ -Fe₅C₂(510) is circled by the red dotted lines. Purple, gray and orange balls denote Fe, C, and Cu atoms, respectively.

The potential energy profile of $CH_x + CH_x$ (x = 1, 2) coupling and CO insertion into CH_x (x = 1, 2) reactions on

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Cu⁰- χ -Fe₅C₂(510) in comparison to χ -Fe₅C₂(510) is presented in Figure 6a. The activation barriers for C₂-hydrocarbons (C₂H₂/C₂H₄) and C₂-oxygenates (CHCO/CH₂CO) formation over Cu⁰- χ -Fe₅C₂(510) are remarkably lower than those on χ -Fe₅C₂(510), especially for CHCO/CH₂CO formation, suggesting that Cu⁰- χ -Fe₅C₂(510) exhibits a higher catalytic activity towards the formation of

C₂-hydrocarbons and C₂-oxygenates in comparison to χ -Fe₅C₂(510). The activation barrier difference between C₂H₂(C₂H₄) and CHCO(CH₂CO) formation decreases to 44.7(18.5) kJ·mol⁻¹ on Cu⁰- χ -Fe₅C₂(510) from 108.6(65.1) kJ·mol⁻¹ on χ -Fe₅C₂(510), indicating that the selectivity of C₂-oxygenates on Cu⁰- χ -Fe₅C₂(510) are higher than that on χ -Fe₅C₂(510), especially for CH₂CO formation.



Figure 6. (a) The potential energy profiles of $CH_x + CH_x$ (x = 1, 2) coupling and CO insertion into CH_x (x = 1, 2) on χ -Fe₅C₂(510) and Cu⁰- χ -Fe₅C₂(510), respectively. (b) Projected densities of states for the surface *d*-orbital center of Cu-Fe, Fe, and Rh over Cu⁰- χ -Fe₅C₂(510), χ -Fe₅C₂(510), and Rh(111), respectively, where the vertical black dashed lines denote the *d*-band center and the vertical blue dashed line is the Fermi level. It is noted that for calculating the *d*-band center, surface Fe and Cu atoms are selected over Cu⁰- χ -Fe₅C₂(510), surface Fe atoms and Rh atoms are selected over χ -Fe₅C₂(510) and Rh(111) surface, respectively. (c) Top view and (d) side view of the charge density difference of Cu⁰ atoms for Cu⁰- χ -Fe₅C₂(510) surface. The blue and yellow shaded regions denote electronic charge depletion and charge accumulation, respectively. Purple, gray, and orange balls denote Fe, C, and Cu atoms, respectively.

The Electronic Effect of Cu⁰-x-Fe₅C₂(510). The geometric structure of the catalytic active site is intrinsically linked to its electronic structure.³ To gain a deep insight into the electronic effect of $Cu^0 - \chi - Fe_5C_2(510)$, we conducted the calculation of projected densities of states (PDOS), *d*-band center (ε_d : the average energy of the *d*-band), charge density difference, and Bader charge. The ε_d characterizes the ability to eject an electron to the adsorbate from the *d*-band of the metal.⁴⁶ The electronic effect on the binding strength of adsorbate attributes to the change in the electronic structure of a catalyst. For transition metals, the way their *d*-band interacts with the adsorbate determines the binding strength.^{3,44} The trend is that the more low-lying (relative to the Fermi level) the d-band, the weaker the binding owing to the occupancy of antibonding states.^{3,44}

The PDOS for the ε_d of metallic Cu-Fe, Fe, and Rh on Cu⁰- χ -Fe₅C₂(510), χ -Fe₅C₂(510), and Rh(111) surfaces are shown in Figure 6b. The ε_d of Cu⁰- χ -Fe₅C₂(510) surface is 0.09 eV closer to the Fermi level than that of χ -Fe₅C₂(510)

surface (Figure 6b). For CO insertion into CH_x to C_2 oxygenates, a C–C bond is formed when the CH_x species migrate to CO, the doubly occupied 5σ CO orbital interacts with the doubly occupied σ -CH_x orbitals to generate doubly occupied bonding and anti-bonding orbitals, thereby giving the repulsion.⁴⁷ The upward shift of ε_d on Cu⁰- χ - $Fe_5C_2(510)$ surface (Figure 6b) empties more anti-bonding states, which could accept more electrons from CO and CH_x fragments orbitals than that on χ -Fe₅C₂(510) surface, thereby reducing the repulsion and facilitating CO insertion into CH_x.^{3,47} In addition, the downward shift of ε_d (0.38 eV) on Rh(111) surface (Figure 6b) can accept less electrons from CO and CH_x fragments orbitals than that on $Cu^0-\chi$ -Fe₅C₂(510) surface, thereby increasing the repulsion and retarding CO insertion into CH_x,^{3,47} in line with that CO insertion into $CH_x(x = 1, 2)$ to C₂-oxygenates on Rh(111) surface⁴⁵ has higher activation barriers (Table S9) than those on $Cu^0 - \chi - Fe_5C_2(510)$ surface.

The calculated density of states shows that χ -Fe₅C₂ is metallic in nature (Figure S27), where Fe is a cation with a

Bader charge of 0.40 *e*, and C is anion with Bader charge of $-0.99 \ e$. The plotted charge density difference of Cu⁰ atoms for Cu⁰– χ -Fe₅C₂(510) surface with top view and side view in Figure 6c–d indicates that the electron-rich interface of Cu⁰– χ -Fe₅C₂(510) is due to the delocalized electron transfer from Cu⁰ atoms, which facilitates CO activation and CO insertion into CH_x (x = 1-3) to C₂-oxygenates at the interface of Cu⁰– χ -Fe₅C₂(510).^{48,49} Indeed, the delocalized electron transfer from Cu⁰ atoms for Cu⁰– χ -Fe₅C₂(510) is also confirmed by calculating Bader charge analysis of Cu⁰ atoms for Cu⁰– χ -Fe₅C₂(510) with a positive charge of 0.08 *e*.⁴⁹ Therefore, the synergistic geometric and electronic effects of Cu⁰– χ -Fe₅C₂ binary catalyst account for the increased activity and selectivity towards C₂-oxygenates in comparison to χ -Fe₅C₂ and Rh catalyst.

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59 60 The Quantitative Energy Descriptor for Catalytic Activity and Selectivity. To quantify the activity and selectivity for CO hydrogenation to C₂-hydrocarbons and C₂oxygenates, we calculated the effective barriers $(E_{\text{eff,CH}_x+CH_x} \text{ and } E_{\text{eff,CH}_x+CO})$ to evaluate the reaction rate $(r_{\text{CH}_x+CH_x} \text{ and } r_{\text{CH}_x+CO})$ of CH_x + CH_x (x = 1, 2) coupling and CO insertion into CH_x (x = 1, 2). Additionally, we calculated the effective barrier difference ($\Delta E_{\text{eff}} = E_{\text{eff,CH}_x+CH_x} - E_{\text{eff,CH}_x+CO}$) between CH_x + CH_x (x = 1, 2) coupling and CO insertion into CH_x (x = 1, 2) to describe the selectivity between C₂-hydrocarbons and C₂-oxygenates. In principle, the higher ΔE_{eff} represents the higher selectivity of C₂oxygenates and the lower selectivity of C₂-hydrocarbons. Furthermore, the coverage of C₁ species CH_x (x = 1, 2) (θ_{CH_x}) and CO (θ_{CO}) is considered.

Table 1. The effective barrier (E_{eff}) of CH_x + CH_x (x = 1, 2) coupling and CO insertion into CH_x (x = 1, 2), and the effective barrier difference (ΔE_{eff}) between CH_x + CH_x coupling and CO insertion into CH_x (x = 1, 2) on χ -Fe₅C₂(510) and Cu⁰- χ -Fe₅C₂(510), respectively. (Unit: kJ·mol⁻¹)

	CH species		CH ₂ species	
	χ-Fe ₅ C ₂ (510)	Cu ⁰ -x-Fe ₅ C ₂ (510)	χ-Fe ₅ C ₂ (510)	Cu ⁰ -x-Fe ₅ C ₂ (510)
$E_{\rm eff,CH_x+CH_x}$	48.9	41.2	241.3	227.9
$E_{\rm eff,CH_x+CO}$	151.0	75.3	209.8	139.4
$\Delta E_{\rm eff}$	-102.1	-34.1	31.5	88.5

The effective barriers (E_{eff}) of CH coupling to C₂H₂ and CH_2 coupling to C_2H_4 are 48.9 and 241.3 $kJ{\cdot}mol^{-1}$ on $\chi{\cdot}$ $Fe_5C_2(510)$ (Table 1), which decrease to 41.2 and 227.9 kJ·mol⁻¹ on Cu⁰- χ -Fe₅C₂(510), respectively. This indicates that the formation rate of (C_2H_2/C_2H_4) is slightly improved on Cu⁰-x-Fe₅C₂(510) compared with x-Fe₅C₂(510). Interestingly, the effective barriers of CO insertion into $CH_x(x =$ 1, 2) remarkably decrease to 75.3 and 139.4 kJ·mol⁻¹ on Cu⁰-x-Fe₅C₂(510) from 151.0 and 209.8 kJ·mol⁻¹ on x-Fe₅C₂(510) (Table 1), respectively. This suggests that the formation rate of CH_xCO (x = 1, 2) can be significantly enhanced on $Cu^0-\chi$ -Fe₅C₂(510) compared with χ -Fe₅C₂(510). More importantly, the effective barrier differences (ΔE_{eff}) between $CH_x + CH_x$ (x = 1, 2) coupling and CO insertion into CH_x (x = 1, 2) on $Cu^0 - \chi - Fe_5C_2(510)$ are much higher by 68.0 and 57.0 kJ·mol⁻¹ than those on χ -Fe₅C₂(510) (Table 1), respectively, confirming that $Cu^0 - \chi - Fe_5C_2(510)$ significantly improves the C₂-oxygenates selectivity.

Reaction Pathway on Cu⁰–\chi-Fe₅C₂(510). The formation of C₂-oxygenates is preferred by CO insertion into CH_x(x =1, 2) on Cu⁰– χ -Fe₅C₂(510) (Figures S24–S26), subsequently, C₂-oxygenates undergo a stepwise hydrogenation to C₂H₅OH (Figure 7a). The proposed reaction pathway for CO hydrogenation to C₂H₅OH over Cu⁰– χ -Fe₅C₂(510) is shown in Figure 7a and Supplementary Movie 2. The potential energy profile with calculated structural parameters of initial states (ISs) and final states (FSs), and transition states (TSs) in the reaction pathway are displayed in Figure 7a–b. The catalytic elementary steps, activation barriers and reaction energies are listed in Table S10.

Starting from CHCO intermediate (Figure 7a), one reaction pathway is CHCO hydrogenation [CHCO+H(1)] to CH₂CO via **TS1** with an activation barrier and reaction energy of 37.5 and 24.1 kJ·mol⁻¹, respectively; in **TS1**, CHCO is adsorbed at the 3-fold F₁2 site of Fe–Cu interface, and H atom is adsorbed at the top T3 Fe site with the C–H distance of 1.693 Å. The other is CHCO hydrogenation [CHCO+H(2)] to CHCHO via **TS2** with an activation barrier and reaction energy of 74.6 and 5.9 kJ·mol⁻¹, respectively. Thus, CHCO prefers hydrogenation to CH₂CO.

Starting from CH₂CO, one reaction pathway is CH₂CO hydrogenation [CH₂CO+H(1)] to CH₃CO via **TS3** with an activation barrier and reaction energy of 34.5 and -3.1 kJ·mol⁻¹, respectively; in **TS3**, CH₂CO is adsorbed at the 3-fold F₁1 site of Fe–Cu interface, H atom is adsorbed at the top T4 Fe site, and the C–H distance decreases to 1.476 Å from 2.585 Å in CH₂CO+H(1). The second one is CH₂CO hydrogenation [CH₂CO+H(2)] to CH₂CHO via **TS4** with an activation barrier and reaction energy of 92.9 and -66.1 kJ·mol⁻¹, respectively. The third one is CH₂CO hydrogenation CH₂CO+H(3) to CH₂COH via **TS5** with an activation barrier and reaction energy of 128.1 and 76.1 kJ·mol⁻¹, respectively. Thus, CH₂CO prefers hydrogenation to CH₃CO.

Starting from CH₃CO, one reaction pathway is CH₃CO hydrogenation [CH₃CO+H(1)] to CH₃CHO via **TS6** with an activation barrier and reaction energy of 47.1 and-14.5 kJ·mol⁻¹, respectively; in **TS6**, CH₃CO is adsorbed at the 3-fold F₁1 site of Fe–Cu interface, H atom is adsorbed at the Fe–Fe bridge site, and the C–H distance decreases to 1.528 Å from 2.188 Å in CH₃CO+H(1). The other reaction pathway is CH₃CO hydrogenation [CH₃CO+H(2)] to CH₃COH via **TS7** with an activation barrier and reaction energy of 140.7 and 87.8 kJ·mol⁻¹, respectively.

As CH₃CO prefers hydrogenation to CH₃CHO via TS6, subsequently, CH₃CHO hydrogenation [CH₃CHO+H(1)] to CH₃CH₂O via TS8 has an activation barrier of 40.8 kJ·mol⁻¹ and a reaction energy of -28.4 kJ·mol⁻¹, which is more favorable than CH₃CHO hydrogenation [CH₃CHO+H(2)] to CH₃CHOH via **TS9** with an activation barrier and reaction energy of 155.8 and 36.2 kJ·mol⁻¹, respectively; in TS8, CH₃CHO is adsorbed at the B9 Cu-Cu bridge site of Fe-Cu interface, H atom is adsorbed at the top T₁5 site of Fe-Cu interface, and the C-H distance reduces to 1.631 Å from 2.859 Å in CH₃CHO+H(1). Eventually, CH₃CH₂O hydrogenation to C₂H₅OH via **TS10** is exothermic by 11.1 kJ·mol⁻¹ with an activation barrier of 114.2 kJ·mol⁻¹; in TS10, CH₃CH₂O is adsorbed at the top T₁7 Cu site of Fe-Cu interface, H atom is adsorbed at the B12 Cu-Cu bridge site of Fe-Cu interface, and the O-H distance decreases to 1.680 Å from 3.531 Å in CH₃CH₂O+H.

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Figure 7. The reaction pathway for CO hydrogenation to C_2H_5OH on $Cu^0-\chi$ -Fe₅C₂(510) surface proposed from DFT calculation. (a) The reaction pathway and potential energy profile with calculated structural parameters of initial states and final states. (b) Transition states in the reaction pathway. Bond lengths are in Å. Orange ball denotes Cu atom; Purple and gray balls denote Fe and C atoms of χ -Fe₅C₂(510), respectively; Dark green, red, and white balls denote C, O, and H atoms of adsorbates, respectively.

CONCLUSION

In summary, we advocate that the synergistic geometric and electronic interactions determine the activity of $Cu^0 - \chi - Fe_5C_2$ for selective CO hydrogenation to higher alcohols, outperforming than silica-supported precious Rhbased catalysts, by using a combination of experimental evidence from bulk, surface-sensitive, and imaging techniques collected on real and high-performance Cu-Fe binary catalytic systems coupled with DFT calculations. The closer the *d*-band center of $Cu^0 - \chi$ -Fe₅C₂(510) surface to the Fermi level than those of χ -Fe₅C₂(510) and Rh(111) surface (0.09 and 0.38 eV, respectively), and the elecronrich interface of $Cu^0 - \chi - Fe_5C_2(510)$ owing to the delocalized electron transfer from Cu⁰ atoms, which thereby promote CO activation and CO insertion into alkyl species to C2oxygenates at the interface of $Cu^0-\chi$ -Fe₅C₂(510) and thus improve C₂H₅OH selectivity. Starting from CHCO intermediate, the proposed reaction pathway for CO hydrogenation to C_2H_5OH on $Cu^0 - \chi - Fe_5C_2(510)$ is $CHCO+(H)\rightarrow CH_2CO+(H)\rightarrow CH_3CO+(H)\rightarrow CH_3CHO+(H)\rightarrow CH_3C$ $H_2O+(H) \rightarrow C_2H_5OH$. This study may pave a way for the rational design of high-performance binary catalysts made from earth-abundant metals with synergistic interaction for tuning selectivity.

EXPERIMENTAL PROCEDURES

Catalyst Synthesis. 3DOM Cu-Fe catalysts were prepared by poly(methyl methacrylate) (PMMA) colloidal crystal template (CCT) method,²¹ using ethylene glycol (EG)-methanol solution of metal nitrates Cu(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O as precursors. Mono-disperse PMMA microspheres were synthesized using an emulsion technique. The PMMA was centrifuged to form CCT. The stoichiometric amounts of mixed metal nitrates were dissolved with 15 mL of EG by stirring in a beaker (100 mL) at RT for 2 h, and the mixed solution was poured into a volumetric flask (50 mL). Methanol (6 mL) and EG were added to achieve the solution with 12 vol.% of methanol. The mixed Cu-Fe precursor was added to CCT, permeated the voids between the close-packed spheres, and condensed into a hard and inorganic framework upon frying. Excessive liquid was removed from the impregnated CCT via a Buchner funnel connected to vacuum. The infiltered template was dried in a desiccator at RT overnight. Finally, the dried sample was mixed with γ -alumina sphere (0.125 inch) and heated in a quartz tube at 1 °C min⁻¹ from RT to 450 °C in air flow for 5 h. The y-alumina sphere helped the removal of heat produced by oxidative decomposition of PMMA during the calcination, and it was separated from the catalyst after calcination and discarded.

Measurements of Catalytic Performance. The catalytic tests were carried out in a half-inch fixed-bed reactor. 1 g catalyst diluted with quartz sand was loaded in the catalyst bed. First, the catalysts were *in situ* reduced at atmospheric pressure by passing with $H_2/CO = 1.0$. During *in situ* reduction process, the temperature was increased to 300 °C and maintained for 48 h. Second, the temperature was lowered to 25 °C with syngas ($H_2/CO = 1, 6\% N_2$ as internal standard) and the reactor pressure was slowly in-

creased to 700 psig. Then, the temperature in the catalyst bed was increased from 25 °C to the target temperature (e.g. 260 °C). Once the target temperature was achieved, the reaction was proceeded for a period of 10–15 h to ensure steady state of the catalyst activity. The time-on-stream after achieving steady state is 120 h.

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The outlet gaseous products were analyzed on-line using Agilent 7890 gas chromatograph (GC) provided with two thermal conductivity detectors (TCD) and a flame ionization detector (FID). C1-C4 ranged alkanes and alkenes were analyzed using a HP Plot capillary column (50 m \times 530 μ m ID) with a FID and N₂ carrier. CO, CO₂, and N₂ were analyzed using molecular sieve-packed columns with TCD and He carrier. H₂ was analyzed using molecular sieve-packed columns with TCD and N2 carrier. Liquid products were collected using a cold trap kept at -5 °C. Alcohols and hydrocarbons were analyzed off-line using a GC coupled to a mass spectrometer (GC-MS) equipped with an Agilent 6890 Series gas chromatograph system, an Agilent 7683B Series Injector, a 5973 Mass Selective Detector, and a FID detector. An Agilent DB-WAXetr (50 m×0.32 mm I.D., 1.0µm) capillary column was used for analyzing aqueous product that included oxygenated compounds and water, and water was quantified using an external standard method. An Agilent HP-5 capillary column was used for analyzing hydrocarbons.

C0 conversion (%) was defined as: C0 conversion (%) = $\frac{F_{in}X_{CO,in} - F_{out}X_{CO,out}}{F_{in}X_{CO,in}} \times 100$, where F_{in} and F_{out} (mol h⁻¹) were the total molar flow rates of the reactor inlet syngas and outlet gas, respectively, $X_{(i),in}$ and $X_{(i),out}$ are the molar fraction of component *i* in the reactor inlet syngas and outlet gas, respectively. Product selectivity was defined as: Selectivity (mol%) = $\frac{n_j F_{out} X_j}{F_{in} X_{CO,in} - F_{out} X_{CO,out}} \times 100$, where n_j represents the number of carbon atoms contained in product *j*, and X_j represents the molar fraction of product *j*. The formation rate of C₂₊OH was defined as: $r_{C_{2+}OH}(mmol g^{-1}_{cat}, h^{-1}) = \frac{C_{2+}OH(mmol)}{Weight of Catalyst (g) \times Time (h)}$.

Mössbauer Spectroscopy. Mössbauer experiments were conducted using a ⁵⁷Co/Rh source in a constant acceleration transmission spectrometer. The spectra were recorded at 27 °C. The spectrometer was calibrated using a standard α -Fe foil and the reported isomer shifts were relative to the center of the α -Fe spectrum. The WinNormos-for-Igor 3.0 program was used to determine Mössbauer parameters. A nonlinear least-squares fitting procedure with a set of independent Lorentzian lines that models the spectra as a combination of singlets, quadruple doublets and/or magnetic sextets was used for data analysis. The spectra components were identified based on their isomer shift, quadruple splitting, and magnetic hyperfine field. Magnetic hyperfine fields were calibrated with 330 kOe field of α -Fe at 27 °C.

Cs-corrected HAADF-STEM Imaging and EELS Elemental Mapping. HAADF-STEM images were taken by a JEOL ARM 200 equipped with a probe corrector and a cold field emission gun operated at 200 eV with a spatial resolution of 0.08 nm, and EELS elemental maps were taken by using Gatan Quantum 965 with an energy resolution of 0.6 eV without a monochromator.

In situ Ambient Pressure X-ray Photoelectron Spectroscopy. Gas flowed through the reactor and exited through the exit port and an aperture that interfaces the gaseous environment of the pre-lens. Flow rate in the reactor was measured using a mass flow meter installed between each gas source and the entrance of the flow reaction cell. The flow rate of pure gas was in the range of 3– 5 mL pure gas per minute. The total pressure of the mixture gas of reactor was measured using a capacitance gauge installed at the entrance. The pressure at the exit was measured using another capacitance gauge. An average of the pressures at entrance and exit was defined as the pressure above the catalyst in the catalytic reactor that was integrated with a monochromatic Al K α (hu = 1486.7 eV) X-ray source and a different pumping stage.

The catalyst was heated by heating the vacuum side of a sample stage using e-beaming heater installed in the vacuum section between the external wall of the catalytic reactor and the internal wall of the UHV chamber. The gaseous side was the internal wall of the reactor. Au thin film (0.4 mm thick, 99.99%, VWR) was used as a substrate to load a catalyst. Au foil was deliberately roughened using a SiC knife to increase adhesion. A certain amount of 3DOM Cu₂Fe₁ catalyst was suspended in 100% ethanol and deposited on pre-cleaned Au foil. Ethanol left in the sample on the Au foil was vaporized by placing Au foil in a vacuum oven at 60°C. The *in situ* reaction medium was syngas (H₂/CO = 1). The reaction pressure was 1 mbar. The temperature varied from RT to 500°C, and each target temperature was held for 1 h before spectrum collection. High resolution spectra of Cu 2p, Cu (LMM), Fe 2p, and C 1s were gathered using an average of 5–35 scans with a pass energy of 23.5 eV and a step size of 0.05 eV. All spectra were calibrated to Au 4f_{7/2} binding energy (84.0 eV).

In situ X-ray Absorption Spectroscopy. In situ XAS measurements were performed at beamline 9-BM-C of the Advanced Photon Sources at Argonne National Laboratory. All Cu K-edge and Fe K-edge measurements were carried out in transmission mode. A copper or iron foil spectrum was acquired through a third ion chamber simultaneously with each measurement for energy calibration. Harmonic rejection was accomplished using a Rhodiumcoated harmonic rejection mirror. The CuO, Cu₂O, Fe₃O₄, and γ -Fe₅C₂ standards, and catalyst samples were diluted with boron nitride (BN) then pressed into a pellet, which could simultaneously hold six samples. The sample thickness was chosen to give a total absorbance (µx) at Cu K-edge or Fe K-edge between 1 and 2 absorption lengths, and edge steps ($\Delta \mu x$) around 0.3–0.5. For *in* situ measurements, the sample holder was placed into a controlled atmosphere quartz tube, equipped with thermocouple to monitor the temperature of samples, Swagelok Ultra-Torr fitting and Kapton windows for sealing, and shut-off valves for gas treatments and isolation of the samples after in situ treatment. The quartz tube was placed within a tube furnace controlled by a programmable temperature controller. The sample was heated from RT to 400 °C at a rate of 3°C min-1 under a 10 mL min-1 flow of $3\%H_2/3\%CO$ balanced with helium, and held at each desired temperature for 1 h except 300°C for 24 h. Data were acquired at RT in helium flow. Trace oxidants in helium were removed by passing through a Matheson PURO Gas Triple Purifier Cartridge. The IFEFFIT package was used for data normalization and processing.50,51 The normalized, energy-calibrated XANES spectra were obtained by standard methods. Standard procedures based on IFEFFIT were used to process the EXAFS data.

COMPUTATIONAL METHODOLOGY

All calculations were performed by using the Vienna Ab Initio Simulation Package (VASP),52,53 in which the electron-ion interactions were expressed by projector-augmented wave (PAW) method.54,55 The generalized gradient approximation (GGA) proposed by Perdew-Burke-Ernzerhof (PBE)56,57 was used to describe the exchange-correlation energies and potential. Owing to the magnetic properties of Fe, all calculations were spin-polarized⁵⁸ with a plane wave cutoff energy of 400 eV. The Brillouin zone was sampled by a 2×2×2 k-points grid generated via the Monkhorst-Pack procedure.^{59,60} The geometry optimization was converged when the energy differences between two electronic optimization steps were smaller than 10⁻⁵ eV, and the forces for ions were less than 0.03 eV/Å. To study the minimum energy reaction pathways, the Climbing-Image Nudged Elastic Band method (CI-NEB)61,62 was employed to find saddle points between the known reactants and products, and the transition states were optimized using the dimer method.^{63,64} Bader charge analysis⁶⁵ and charge density difference analysis⁶⁶ was conducted for discussing charge transfer. The optimized transition state structures were converged when the forces for all atoms were less than 0.05 eV/Å. In all calculated energy data, the zero-point energy (ZPE) has been considered.

 χ -Fe₅C₂ has a monoclinic structure with C2/c crystallographic symmetry,⁶⁷ including 20 Fe and 8 C atoms per unit cell. The cal-

culated lattice parameters (a = 11.588 Å, b = 4.579 Å, c = 5.059 Å, and β =97.7°) and magnetic moment (1.73 µB) agree well with the previous experimental data.^{68,69} The χ -Fe₅C₂(510) is modeled using a $p(2\times1)$ supercell slab with three-layered iron and sixlayered carbon. For χ -Fe₅C₂(510) and Cu⁰- χ -Fe₅C₂(510) surface models, the bottom one-layered iron and two-layered carbon are fixed in their bulk position during all the calculations, whereas the top two-layered iron, four-layered carbon, and adsorbates are relaxed. The vacuum spacing between slabs is 10 Å to ensure no significant interaction between the slabs.

The *d*-band center (ε_d) is calculated via Eq. (1),⁴⁶ where ρ_d represents the density of states projected onto the metal atom's *d*-band and E_f is the Fermi energy.

$$\varepsilon_d = \frac{\int_{-\infty}^{E_f} E_{P_d}(E) dE}{\int_{-\infty}^{E_f} P_d(E) dE}$$
(1)

Based on the DFT calculation results, adsorption energies, reaction energies, and activation barriers are used to describe the thermodynamic and kinetic properties of the reaction. The adsorption energy is defined as Eq. (2), where $E_{(adsorbates/slab)}$ is the total energy of the slab with adsorbates, $E_{(slab)}$ is the total energy of the slab, and $E_{(adsorbates)}$ is the total energy of free adsorbates. Therefore, the more negative the E_{ads} , the stronger the adsorption. The reaction energy (ΔH) and activation barrier (E_a) are calculated by Eqs. (3) and (4), respectively, where E(IS), E(FS), and E(TS)are the energies of the corresponding initial state (IS), final state (FS), and transition state (TS), respectively.

$$E_{ads} = E_{(adsorbates/slab)} - [E_{(slab)} + E_{(adsorbates)}]$$
(2)

$$\Delta H = E(FS) - E(IS)$$
(3)

$$E_a = E(TS) - E(IS)$$
(4)

The coverage of C₁ species CH_x (*i* =1, 2) (θ_{CH_x}) can be expressed with respect to the C coverage⁷⁰ ($\theta_{\rm C}$) by Eq. (5), where E_x is the relative stability of CH_x with respect to C on surfaces, which is the energy difference between adsorbed CH_x and C + xH; t is $\theta_{\rm H}/\theta_*, \theta_{\rm H}$ and θ_* are the coverage of H and free surface site, respectively. Based on the previous DFT calculation studies,71-75 the reaction rate of $CH_x + CH_x$ (x = 1, 2) coupling and CO insertion into CH_x (x = 1, 2) can be derived and expressed as Eqs. (6) and (7), respectively, where $E_{\text{eff,CH}_x+\text{CH}_x} = E_a^{\text{CH}_x+\text{CH}_x} + 2E_x$, and $E_{\text{eff,CH}_x+\text{CO}} = E_a^{\text{CH}_x+\text{CO}} + E_x$ are the effective barriers of $\text{CH}_x + \text{CH}_x$ (x = 1, 2) coupling and CO insertion into CH_x (x = 1, 2) reactions, respectively. $E_a^{CH_x+CH_x}$ and $E_a^{CH_x+CO}$ are the activation barriers of $CH_x + CH_x$ (x = 1, 2) coupling and CO insertion into CH_x (x = 1, 2) reactions, respectively. Combining Eqs. (6) and (7), the ratio of reaction rate for the $CH_x + CH_x$ (x = 1, 2) coupling and CO insertion into $CH_x(x = 1, 2)$ reactions can be expressed as Eq. (8), where $\Delta E_{\text{eff}} = E_{\text{eff,CH}_x + \text{CH}_x} - E_{\text{eff,CH}_x + \text{CO}}$ is the effective barrier difference between $CH_x + CH_x$ (x = 1, 2) coupling and CO insertion into CH_x (x = 1, 2) reactions. It is noteworthy that both t and $\frac{\theta_c}{\theta_{co}}$ have little effect on the selectivity^{74,75} in comparison to ΔE_{eff} with exponential impact. Thus, $\Delta E_{\rm eff}$ can be used as a quantitative energy descriptor to evaluate the FTS selectivity between $CH_x + CH_x$ (x = 1, 2) coupling and CO insertion into CH_x (x = 1, 2) reactions. In principle, the higher ΔE_{eff} represents the higher selectivity of C₂oxygenates and the lower selectivity of C2-hydrocarbons.

$$\theta_{\mathrm{CH}_{x}} = e^{\left(-\frac{E_{x}}{RT}\right)}\theta_{\mathrm{C}}(\theta_{\mathrm{H}}/\theta_{*})^{x} = e^{\left(-\frac{E_{x}}{RT}\right)}\theta_{\mathrm{C}}t^{x}$$
(5)
$$r = -A_{\mathrm{C}}\left(-\frac{E_{a}^{\mathrm{CH}_{x}+\mathrm{CH}_{x}}}{RT}\right)a^{2} = -A_{\mathrm{C}}\left(-\frac{E_{a}^{\mathrm{CH}_{x}+\mathrm{CH}_{x}}+2E_{x}}{RT}\right)a^{2} + 2x$$

$$= Ae^{\left(-\frac{E_{eff,CH_x+CH_x}}{RT}\right)}\theta_C^2 t^{2x}$$
(6)

$$r_{\rm CH_x+CO} = Ae^{\left(-\frac{E_a^{\rm CH_x+CO}}{RT}\right)} \theta_{\rm CH_x} \theta_{\rm CO} = Ae^{\left(-\frac{E_a^{\rm CH_x+CO}+E_x}{RT}\right)} \theta_{\rm C} \theta_{\rm CO} t^x$$

$$= Ae^{\left(\frac{RT}{RT}\right)}\theta_{C}\theta_{CO}t^{\chi}$$
(7)
$$\frac{r_{CH_{\chi}+CH_{\chi}}}{r_{CH_{\chi}+CO}} = t^{\chi}\frac{\theta_{C}}{\theta_{CO}}e^{\left(-\frac{\Delta E_{eff}}{RT}\right)}$$
(8)

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:.

Catalyst characterizations, catalytic performance data, DFT calculation results, additional experimental methods, including SI Figures S1–S27 and Tables S1–S10 (PDF)

Supplementary Movies, showing the optimum reaction pathway from proposed DFT for CO hydrogenation on χ -Fe₅C₂(510) and Cu⁰- χ -Fe₅C₂(510) surface (AVI)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Shi, J. Chem. Rev., 2013, 113, 2139-2181.

(2) Yu, W.; Porosoff, M. D.; Chen, J. G. *Chem. Rev.*, **2012**, *112*, 5780–5781.

(3) Nørskov, J. K.; Bligaard, T.; Rossmeisl, J.; Christensen, C. H. *Nat. Chem.*, **2009**, *1*, 37–46.

(4) Strasser, P.; Koh, S.; Anniyev, T.; Greeley, J.; More, K.; Yu, C.; Liu, Z.; Kaya, S.; Nordlund, D.; Ogasawara, H.; Toney, M. F.; Nilsson, A. *Nat. Chem.*, **2010**, *2*, 454–460.

(5) Prieto, G.; Beijer, S.; Smith, M. L.; He, M.; Au, Y.; Wang, Z.; Bruce, D. A.; de Jong, K. P.; Spivey, J. J.; de Jongh, P. E. *Angew. Chem. Int. Ed.*, **2014**, *53*, 6397–6401.

(6) Pei, Y. -P.; Liu, J. -X.; Zhao, Y. -H.; Ding, Y. -J.; Liu, T.; Dong, W. -D.; Zhu, H. -J.; Su, H. -Y.; Yan, L.; Li, J. -L.; Li, W. -X. *ACS Catal.*, **2015**, *5*, 3620–3624.

(7) Xiang, Y.; Kruse, N. Nat. Commun., 2016, 7, 13058.

(8) Torres Galvis, H. M.; Bitter, J. H.; Khare, C. B.; Ruitenbeek, M.; Iulian Dugulan, A.; de Jong, K. P. *Science* **2012**, *335*, 835–838.

(9) Behrens, M.; Studt, F.; Kasatkin, I.; Kühl, S.; Hävecker, M.; Abild-Pedersen, F.; Zander, S.; Girgsdies, F.; Kurr, P.; Kniep, B. -L.; Tovar, M.; Fischer, R. W.; Nørskov, J. K.; Schlögl, R. *Science* **2012**, *336*, 893–897.

(10) Xiang, Y.; Chitry, V.; Liddicoat, P.; Felfer, P.; Cainey, J.; Ringer, S.; Kruse, N. *J. Am. Chem. Soc.*, **2013**, *135*, 7114–7117.

- (11) Luk, H. T.; Mondelli, C.; Ferré, D. C.; Stewart, J. A.; Pérez-Ramírez, J. *Chem. Soc. Rev.*, **2017**, *46*, 1358–1426.
- (12) Wang, D.; Chen, B.; Duan, X.; Chen, D.; Zhou, X. *J. Energy Chem.*, **2016**, *25*, 911–916.

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5

6

7

8

9

13

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34

- (13) Zhong, L.; Yu, F.; An, Y.; Zhao, Y.; Sun, Y.; Li, Z.; Lin, T.; Lin, Y.; Qi, X.; Dai, Y.; Gu, L.; Hu, J.; Jin, S.; Shen, Q.; Wang, H. *Nature* **2016**, *538*, 84–87.
- (14) Yang, C.; Zhao, H.; Hou, Y.; Ma, D. *J. Am. Chem. Soc.*, **2012**, *134*, 15814–15821.
- (15) Mao, W.; Su, J.; Zhang, Z.; Xu, X. -C.; Dai, W.; Fu, D.; Xu, J.; Zhou, X.; Han, Y. -F. *Chem. Eng. Sci.* **2015**, *135*, 312–322.
- (16) Mei, D.; Rousseau, R.; Kathmann, S. M.; Glezakou, V. -A.;
 Engelhard, M. H.; Jiang, W.; Wang, C.; Gerber, M. A.; White, J. F.;
 Storage D. I. J. Catal. 2010, 271, 225, 242
- II
 Stevens, D. J. J. Catal., 2010, 271, 325–342.

 12
 (17) Liu, J.; Tao, R.; Guo, Z.; Regalbuto, J. R.; Marshall, C. L.; Klie, R.
 - F.; Miller, J. T.; Meyer, R. J. ChemCatChem **2013**, 5, 3665–3672.
- 14
 (18) Yu, J.; Mao, D.; Han, L.; Guo, Q.; Lu, G. Catal. Commun. 2012,

 15
 27, 1–4.
- 15 27, 1-4.
 (19) Yang, N.; Medford, A. J.; Liu, X.; Studt, F.; Bligaard, T.; Bent, S. F.; Nørskov, J. K. J. Am. Chem. Soc., 2016, 138, 3705–3714.
- (20) Lu, Y.; Yu, F.; Hu, J.; Liu, J. Appl. Catal. A 2012, 429–430, 48–58.
 (21) Lu, Y.; Cao, B.; Yu, F.; Liu, J.; Bao, Z.; Gao, J. ChemCatChem
 2014, 6, 473–478.
- (22) Herranz, T.; Rojas, S.; Pérez-Alonso, F. J.; Ojeda, M.; Terreros,
 P.; Fierro, J. L. G. *J. Catal.*, 2006, 243, 199–211.
 - (23) Kim, K. S. J. Electron. Spectrosc., **1974**, 3, 217–226.
- 22 (24) Svintsitskiy, D. A.; Kardash, T. Y.; Stonkus, O. A.; Slavinskaya,
- 23 E. M.; Stadnichenko, A. I.; Koscheev, S. V.; Chupakhin, A. P.; Boronin, A. I. J. Phys. Chem. C 2013, 117, 14588–14599.
- (25) Natesakhawat, S.; Lekse, J. W.; Baltrus, J. P.; Ohodnicki, Jr., P.
 R.; Howard, B. H.; Deng, X.; Matranga, C. *ACS Catal.*, **2012**, *2*, 1667–1676.
 - (26) Ye, Y.; Wang, L.; Zhang, S.; Zhu, Y.; Shan, J.; Tao, F. *Chem. Commun.*, **2013**, *49*, 4385–4387.
- (27) de Smit, E.; van Schooneveld, M. M.; Cinquini, F.; Bluhm, H.;
 Sautet, P.; de Groot, F. M. F.; Weckhuysen, B. M. *Angew. Chem. Int. Ed.*, 2011, *50*, 1584–1588.
 - (28) Kuivila, C. A.; Butt, J. B.; Stair, P. C. *Appl. Surf. Sci.*, **1988**, *32*, 99–121.
 - (29) Tranquada, J. M.; Heald, S. M.; Moodenbaugh, A. R. *Phys. Rev.* B **1987**, *36*, 5263–5274.
- 35 (30) Kau, L. S.; Hodgson, K. O.; Solomon, E. I. J. Am. Chem. Soc.,
 36 1989, 111, 7103-7109.
- 37 (31) Su, J.; Zhang, Z.; Fu, D.; Liu, D.; Xu, X. -C.; Shi, B.; Wang, X.; Si,
 38 R.; Jiang, Z.; Xu, J.; Han, Y. -F. *J. Catal.*, *2016*, *336*, 94–106.
- (32) Martens, G.; Rabe, P.; Schwentner, N.; Werner, A. *Phys. Rev. B* **1978**, *17*, 1481–1488.
- 40 (33) Sankar, G.; Vasudevan, S.; Rao, C. N. R. *J. Chem. Phys.*, **1986**, 41 85, 2291–2299.
- 42 (34) Wang, X.; Hanson, J. C.; Frenkel, A. I.; Kim, J. Y.; Rodriguez, J. A.
 43 *J. Phys. Chem. B* 2004, *108*, 13667–13673.
- (35) Frenkel, A. I.; Wang, Q.; Marinkovic, N.; Chen, J. G.; Barrio, L.;
 Si, R.; López Cámara, A.; Estrella, A. M.; Rodriguez, J. A.; Hanson, J. C. J. Phys. Chem. C 2011, 115, 17884–17890.
- 46 (36) Bock, D. C.; Pelliccione, C. J.; Zhang, W.; Wang, J.; Knehr, K. W.;
 47 Wang, J.; Wang, F.; West, A. C.; Marschilok, A. C.; Takeuchi, K. J.;
 48 Takeuchi, E. S. ACS Appl. Mater. Interfaces 2016, 8, 11418–11430.
- 49 (37) Thüne, P.; Moodley, P.; Scheijen, F.; Fredriksson, H.; Lancee,
 50 R.; Kropf, J.; Miller, J.; Niemantsverdriet, J. W. H. *J. Phys. Chem. C*,
 2012, *116*, 7367–7373.
- 51 2012, 110, 7307-7373.
 52 (38) Ribeiro, M. C.; Jacobs, G.; Pendyala, R.; Davis, B. H.; Cronauer,
 53 D. C.; Kropf, A. J.; Marshall, C. L. J. Phys. Chem. C, 2011, 115, 478353 4792.
- 54 (39) Park, J. C.; Yeo, S. C.; Chun, D. H.; Lim, J. T.; Yang, J. -I.; Lee, H. 55 T.; Hong, S.; Lee, H. M.; Kim, C. S.; Jung, H. *J. Mater. Chem. A* 2014, 2, 14371–14379.

- (40) Zhai, P.; Xu, C.; Gao, R.; Liu, X.; Li, M.; Li, W.; Fu, X.; Jia, C.; Xie, J.; Zhao, M.; Wang, X.; Li, Y. -W.; Zhang, Q.; Wen, X. -D.; Ma, D. *An-*
- *gew. Chem. Int. Ed.*, **2016**, *55*, 9902–9907. (41) Zhao, S.; Liu, X. -W.; Huo, C. -F.; Li, Y. -W.; Wang, J.; Jiao, H. J. Catal., **2012**, *294*, 47–53.
- (42) Pham, T. H.; Duan, X.; Qian, G.; Zhou, X.; Chen, D. *J. Phys. Chem. C* **2014**, *118*, 10170–10176.
- (43) Olus Ozbek, M.; Niemantsverdriet, J. W. J. Catal., 2014, 317, 158–166.
- (44) Kim, D.; Resasco, J.; Asiri, A. M.; Yang, P. *Nat. Commun.*, **2014**, *5*, 4948.
- (45) Zhao, Y. -H.; Sun, K.; Ma, X.; Liu, J.; Sun, D.; Su, H. -Y.; Li, W. -X. Angew. Chem. Int. Ed., **2011**, *50*, 5335–5338.
- (46) Li, J.; Croiset, E.; Ricardez-Sandoval, L. J. Mol. Catal. A Chem., **2012**, 365, 103–114.
- (47) Choi, Y. M.; Liu, P. J. Am. Chem. Soc., **2009**, 131, 13054–13061.
- (48) van Steen, E.; Claeys, M. *Catal. Struct. React.*, **2015**, *1*, 11–18.
- (49) Tian, X.; Wang, T.; Yang, Y.; Li, Y. -W.; Wang, J.; Jiao, H. *J. Phys. Chem. C* **2015**, *119*, 7371–7385.
- (50) Newville, M. J. Synchrotron. Radiat., **2001**, *8*, 322–324.
- (51) Ravel, B.; Newville, M. J. Synchrotron. Radiat., 2005, 12, 537–541.
- (52) Kresse, G.; Furthmüller, J. Phys. Rev. B **1996**, 54, 11169–11186.
- (53) Kresse, G.; Furthmüller, J. *Comput. Mater. Sci.*, **1996**, *6*, 15–50.
- (54) Blöchl, P. E. Phys. Rev. B **1994**, *50*, 17953–17979.
- (55) Kresse, G.; Joubert, D. *Phys. Rev. B* 1999, *59*, 1758–1775.
 (56) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.*, 1996, *177*, 2005, 2006.
- 77, 3865–3868. (57) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.*, **1997**, 78, 1396.
- (58) Louie, S. G.; Froyen, S.; Cohen, M. L. Phys. Rev. B **1982**, 26, 1738-1742.
- (59) Ge, Q.; Neurock, M.; Wright, H. A.; Srinivasan, N. J. Phys. Chem. B **2002**, *106*, 2826–2829.
- (60) Joos, L.; Filot, I. A. W.; Cottenier, S.; Hensen, E. J. M.; Waroquier, M.; Speybroeck, V. V.; van Santen, R. A. *J. Phys. Chem. C* **2014**, *118*, 5317–5327.
- (61) Sheppard, D.; Xiao, P.; Chemelewski, W.; Johnson, D. D.; Henkelman, G. *J. Chem. Phys.*, **2012**, *136*, 074103.
- (62) Sheppard, D.; Terrell, R.; Henkelman, G. J. Chem. Phys., **2008**, 128, 134106.
- (63) Henkelman, G.; Jónsson, H. J. Chem. Phys., **1999**, 111, 7010–7022.
- (64) Olsen, R. A.; Kroes, G. J.; Henkelman, G.; Arnaldsson, A.; Jónsson, H. J. Chem. Phys., **2004**, *121*, 9776–9792.
- (65) Henkelman, G.; Arnaldsson, A.; Jónsson, H. Comput. Mater. Sci., **2006**, *36*, 354–360.
- (66) Teng, B. -T.; Zhao, Y.; Wu, F. -M.; Wen, X. -D.; Chen, Q. -P.; Huang, W. -X. *Surf. Sci.*, **2012**, *606*, 1227–1232.
- (67) Storsæter, S.; Chen, D.; Holmen, A. Surf. Sci., 2006, 600, 2051–2063.
- (68) Steynberg, P. J.; van de Berg, J. A.; Janse van Rensburg, W. J. Phys.: Condens. Matter **2008**, 20, 064238.
- (69) Retief, J. J. Powder Diffr. **1999**, 14, 130–132.
- (70) Hofer, L. J. E. Cohn, E. M. J. Am. Chem. Soc. **1959**, 81, 1576–1582.
- (71) Cheng, J.; Hu, P.; Ellis, P.; French, S.; Kelly, G.; Lok, C. M. *J. Phys. Chem. C* **2009**, *113*, 8858–8863.
- (72) Cheng, J.; Gong, X. -Q.; Hu, P.; Lok, C. M.; Ellis, P.; French, S. *J. Catal.*, **2008**, *254*, 285–295.
- (73) Cheng, J.; Hu, P.; Ellis, P.; French, S.; Kelly, G.; Lok, C. M. *J. Phys. Chem. C* **2010**, *114*, 1085–1093.
- (74) Pham, T. H.; Qi, Y.; Yang, J.; Duan, X.; Qian, G.; Zhou, X.; Chen, D.; Yuan, W. *ACS Catal.*, **2015**, *5*, 2203–2208.
- (75) Cheng, J.; Hu, P.; Ellis, P.; French, S.; Kelly, G.; Lok, C. M. *J. Phys. Chem. C*, **2008**, *112*, 9464–9473.

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