In Situ Active Site for Fe-Catalyzed Fischer–Tropsch Synthesis: Recent Progress and Future Challenges

Qian-Yu Liu, Cheng Shang,* and Zhi-Pan Liu*

ABSTRACT: Fischer–Tropsch synthesis (FTS) that converts syngas into long-chain hydrocarbons is a key technology in the chemical industry. As one of the best catalysts for FTS, the Fe-based composite develops rich solid phases (metal, oxides, and carbides) in the catalytic reaction, which triggered the quest for the true active site in catalysis in the past century. Recent years have seen great advances in probing the active-site structure using modern experimental and theoretical tools. This Perspective serves to highlight these latest achievements, focusing on the geometrical structure and thermodynamic stability of Fe carbide bulk phases, the exposed surfaces, and their relationship to FTS activity. The current reaction mechanisms on CO activation and carbon chain growth are also discussed, in the context of theoretical models and experimental evidence. We also present the outlook regarding the current challenges in Fe-based FTS.

Fischer–Tropsch synthesis (FTS) is named after German chemists Franz Fischer and Hans Tropsch who succeeded in producing long-chain hydrocarbons from syngas (a mixture of CO and H$_2$) over Fe/ZnO or Co/Cr$_2$O$_3$ catalysts in 1920s. The reaction opens the door for producing oils and chemicals from coals. After one century of extensive research, FTS has been commercialized in large quantity (400 000 barrels per day in the 2010s) around the world using either Fe-based or Co-based catalysts. Fe-catalyzed FTS produces mainly long-chain α-olefins, whereas Co-based FT catalysts yield linear paraffins as primary products. Because of the abundance of Fe in the earth and the better tolerance for feedstocks with lower H$_2$:CO ratio (with water gas shift side reaction), Fe-based FTS catalysts have been the subject of intensive interest in the past decades.

Industrial Fe-based catalysts are operated under high temperatures and pressures, e.g., 423–623 K, 2–3 MPa, and H$_2$/CO = 1–2. The initial catalysts are generally iron oxides or/and hydroxides, which then undergo a long-time activation step (incubation) to become active catalysts. From the 1930s to the 1960s, it began to be realized that several Fe carbide (FeC$_x$) phases are present during FTS in addition to metallic iron (Fe) and iron oxides (FeO$_x$) by ex situ or quasi in situ analysis. The catalyst activation step is thus believed to involve the FeO$_x$ reduction to FeC$_x$ by CO, H$_2$, or syngas under the FTS conditions. To date, various in situ formed FeC$_x$ bulk phases, including FeC, Fe$_3$C, FeC$_2$, FeC$_3$, FeC$_4$, FeC$_5$, FeC$_6$, and FeC$_7$, have been detected according to the X-ray diffraction (XRD) and Mössbauer spectroscopy. These FeC$_x$ phases often coexist as a mixture under FTS conditions, and it is extremely difficult to distinguish their roles in FTS activity.

As early as the 1970s, when surface science techniques became available, CO hydrogenation has been conducted on Fe metal surfaces aiming to provide insights into FTS. Two types of carbon, “carbidic” (atomic) and “graphitic”, were found to grow on the polycrystalline Fe foil, which can be distinguished by quasi in situ Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). The clean iron surfaces are confirmed to be thermodynamically unstable even at ultrahigh-vacuum conditions (below 1 × 10$^{-10}$ mbar) after the treatment of CO and H$_2$ at 1 bar. In the 1990s, four types of carbon species were further distinguished from used iron FT catalysts by temperature-programmed hydrogenation: (i) adsorbed surface atomic carbon, (ii) amorphous surface methylene chains or films, (iii) bulk iron carbide, and (iv) graphitic carbon. Type i atomic carbon was regarded to be responsible for surface polymerization because the initial catalytic activity was found to be positively correlated with the amount of atomic carbon formed on the catalyst surface. The formation of a type iii iron carbide thin layer was pictured recently by using scanning tunneling microscopy (STM) to observe the insertion of C into Fe metal interstices.

However, because of the difficulty of obtaining single-crystal FeC$_x$ phases, the surface chemistry for FeC$_x$ under FTS is still far from being understood. Recent years have seen great advances in probing the active-site structure using modern experimental and theoretical tools. This Perspective serves to highlight these latest achievements, focusing on the geometrical structure and thermodynamic stability of Fe carbide bulk phases, the exposed surfaces, and their relationship to FTS activity. The current reaction mechanisms on CO activation and carbon chain growth are also discussed, in the context of theoretical models and experimental evidence. We also present the outlook regarding the current challenges in Fe-based FTS.
<table>
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<th>phase</th>
<th>symmetry</th>
<th>coordination pattern</th>
<th>formation free energy$^a$ (eV/C atom, µC = −6.90 eV)</th>
<th>XRD (Cu Kα)</th>
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$^a$Formation free energy of FeC phases related to FTS from different characterization techniques.

$^b$Formation free energy of FeC phases related to FTS from different characterization techniques.

$^c$Isomer shift (relative to $\alpha$-Fe)$_x$ mm/s.

$^d$Hyperfine field (T) reference.

$^e$First Fe -- C shell (Å) reference.

$^f$First Fe -- Fe shell (Å) reference.
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<th>XRD (Cu Kα)</th>
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\(^{a}\)TP, triangular prism; O, octahedron. \(^{b}\)Formation free energy calculated by \( \Delta G(\text{FeC}_x) = [G(\text{FeC}_x) - G(\text{Fe}) - x \mu_C]/x \), where \( G(\text{FeC}_x) \) and \( G(\text{Fe}) \) are the Gibbs free energy of the FeC\(_x\) phase and Fe metal (bcc phase). \(^{c}\)Isomer shift relative to the sodium nitroprusside (Na\(_2\)[Fe(CN)\(_5\)NO]•2H\(_2\)O, National Bureau of Standards). \(^{d}\)Mössbauer parameters simulated by theoretical methods (GGA-PBEsol), 0 K. \(^{e}\)Mössbauer parameters simulated by theoretical methods (GGA-PBE), 0 K.
conditions remains largely unknown in experiment. Since the 2000s, density functional theory (DFT) calculations have been popularly carried out for a series of surfaces of Fe metal, Fe₇C₃, θ-Fe₇C₃, ξ-Fe₅C₂, Fe₉C₅, and ε-Fe₂C phases by using the bulk-truncated surface structures.²⁷−⁴⁰ Because different surface models (e.g., surface C and H coverage) were utilized, different reaction mechanisms for CO activation and carbon chain growth have been proposed.²⁹−³³,³⁵−⁴² For CO activation, for example, at least four different mechanisms were reported: (i) direct dissociation over Fe sites; (ii) H-assisted CO dissociation on Fe sites; (iii) CH₃-assisted CO dissociation on C sites of Fe carbide surfaces; and (iv) C-vacancy-mediated direct dissociation on Fe-carbide surfaces.

This Perspective, with a focus on the fundamental aspects of FTS, serves to highlight the latest experimental and theoretical progress on the structural features of FeCₓ bulk and surfaces and their connection to FTS activity. The uncertainties regarding the insitu FeCₓ active site and future challenges for understanding Fe-based FTS will be discussed. Readers interested in the catalyst preparation, applications, and deactivation of Fe-based FTS catalysts may refer to previous reviews.¹³,⁴³−⁴⁵

FeCₓ Bulk Phases. Eight FeCₓ phases at different Fe:C ratios, namely, Fe₂C, Fe₃C, Fe₄C, Fe₅C, Fe₆C, Fe₇C₃, and Fe₈C, have been detected in FTS. Despite the complexity in bulk phases, the local Fe–C coordination patterns are relatively simple, with only two types. The two types are the triangular prism (TP) for θ-Fe₇C₃, ξ-Fe₅C₂, η-Fe₅C₂, θ-Fe₅C₂-II, η-Fe₅C₂, and h-Fe₂C₃ phases and the octahedron (O) for ε’-Fe₂C, ε’-Fe₂C, and η-Fe₂C phases. Obviously, the high C content will favor the octahedron pattern. In Table 1 we list the signatures of these FeCₓ bulk phases in XRD, Mössbauer spectroscopy, and extended X-ray absorption fine structure (EXAFS), including the data from both experiments and theoretical simulations updated based on the previous review by Weckhuysen et al.¹³

The thermodynamic stability of the FeCₓ phases is sensitive to the chemical potential of C (μ_C) that is controlled by the FTS condition (e.g., temperature and pressure of CO and H₂). By conducting DFT calculations on ε-Fe₂C, η-Fe₂C, ε’-Fe₂C, h-Fe₂C₃, ε’-Fe₂C₃, ε’-Fe₂C, and η-Fe₂C phases based on experimental crystal data, de Smit et al. showed the formation energy of various FeCₓ phases is close, i.e., within ~0.1 eV per C atom. They suggested that while Fe₂C and Fe₇C₃ phases are enthalpically most stable during FTS conditions, because of their higher deformation energy of the Fe sublattice (1.6−2.0 × 10⁻² eV/C atom) with respect to Fe (bcc phase) and the higher C concentration, the kinetic factors such as strain and carbon diffusion barrier may inhibit their formation. On the other hand, ε-Fe₂C₃ has the lowest theoretical deformation energy (8.4 × 10⁻³ eV/C atom) and is thus more likely to form during FTS.

By using global neural network (G-NN) potential combined with stochastic surface walking (SSW) global optimization, the global potential energy surface (PES) for FeCₓ phases has been explored recently by our group, and the thermodynamic convex hull for FeCₓ phases at typical FTS conditions (−7.43 ≤ μ_C ≤ −6.60 eV) was constructed,³¹ as shown in Figure 1a. We showed that three bulk phases, namely, Fe₂C₃, Fe₅C₂, and Fe₇C₃, are stable under FTS in producing olefins, where Fe₂C₃ and Fe₇C₃ have rather complex PES with multiple energetically nearly degenerate bulk crystal phases. At high CO conversion, low limit of μ_C, the high Fe:C ratio FeCₓ bulk phases are no longer the convex points and the catalyst becomes FeC₃-dominated.

It is noted that the SSW global structure search³⁶,⁵⁰ identifies a new Fe₂C₃ phase (see Table 1), i.e., o-Fe₂C₃-II,⁵¹ which is the global minimum for Fe₂C₃ composition but has the nearly degenerate formation energy with the known o-Fe₂C₃ (isostructural with Mn₇C₃). Their structures are shown in Figure 1b. The simulated XRD and EXAFS data of o-Fe₂C₃-II are also shown in Table 1 for comparison. The long-suspected Fe₂C₃ phase, h-Fe₂C₃, is thermodynamically unstable according to our formation energy data.

The XRD data (Table 1) show that the major peaks of FeCₓ phases locate in the range of 42−45° (2θ) corresponding to the interplanar spacings from 2.01 to 2.12 Å. For example, for the commonly observed ε-Fe₂C₃, the major peaks are at 44.16°, 43.47°, 45.08°, 40.85°, and 41.17°, which correspond to the crystal planes (510), (021), (312), (112), and (202), respectively. The three phases with the octahedron Fe–C coordination, i.e., ε’-Fe₂C₃, ε-Fe₂C, and η-Fe₂C, have very similar XRD major peaks, manifesting the same hexagonal close packing (hcp) Fe sublattice. They differ mainly in the distribution of C atoms in the octahedral interstices, i.e., randomly distributed in ε’-Fe₂C₃ and ε-Fe₂C, and arranged alternatively along the close-packed line in η-Fe₂C. The regular C distribution leads to the presence of the additional (210) peak at 2θ = 43.76° for η-Fe₂C.

Mössbauer spectroscopy is another important technique to characterize different Fe-containing phases (Fe, FeOx, and FeCₓ). Table 1 lists the Mössbauer data from the literature.⁸,¹⁰,¹₂−¹⁸ It shows that θ-Fe₂C₃, ε-Fe₂C₃, and η-Fe₂C have two, three, and one set of Mössbauer parameters, respectively,
reflecting the number of unique types of Fe atoms in different phases.

This agrees with our theoretical data of the structure fingerprint, which show two (7.27 × 10⁻⁻3 and 1.07 × 10⁻⁻²), three (2.88 × 10⁻⁻³, 3.33 × 10⁻⁻³, and 5.00 × 10⁻⁻³), and one (1.57 × 10⁻⁻ refusing to set of distance-weighted Steinhart order parameter (OP) values for Fe atoms in θ-Fe₅C₂, χ-Fe₅C₂, and η-Fe₅C₂ phases, respectively. For the other Fe₅C₃ phases, there is a lack of consistency in the Mössbauer parameters between theory and experiment. For example, o-Fe₅C₃ exhibits five sets of parameters from the simulation by Liu et al., but there are only four sets of parameters reported in experiment. Interestingly, from our results of Fe OP₂ values, while there are indeed five different types of Fe atoms (OP₂ = 1.71 × 10⁻⁻³, 1.79 × 10⁻⁻³, 1.87 × 10⁻⁻³, 2.81 × 10⁻⁻², and 3.91 × 10⁻⁻²) in o-Fe₅C₃, only four different types of Fe atoms (OP₂ = 1.26 × 10⁻⁻³, 2.28 × 10⁻⁻³, 3.28 × 10⁻⁻³, and 3.75 × 10⁻⁻³) are found in o-Fe₅C₃. No.

DFT functional has been benchmarked on the accuracy of Mössbauer parameters by Liu et al., which shows that the GGA-level DFT functionals, especially PBEsol, succeed in predicting Mössbauer spectra for Fe₅C₃. The higher-level functionals, such as meta-GGA and hybrid functionals, do not necessarily provide improved results based on the comparison using the full-potential linear-augmented plane wave calculations with different functionals (LDA, GGA (PBE, PBEsol, and GGA+U), meta-GGA, and hybrid functionals).

The radial distribution function (RDF) as detected by EXAFS can be utilized to distinguish the Fe–C coordination pattern. The data from both the literature and simulation indicate that Fe₅C₃ with the triangular prism and the octahedron coordination pattern are very different in RDF. Fe₅C₃ with the triangular prism coordination have longer Fe–C distance (1.94–1.99 Å) but shorter Fe–Fe distance (2.52–2.58 Å and 3.60–3.73 Å for first and second shell), compared to the octahedron coordination (1.91, 2.71–2.73, and 3.83–3.90 Å for first Fe–C, first Fe–Fe, and second Fe–Fe shell).

Fe₅C₃ Surfaces. While it is well-accepted that the FT catalyst surfaces decorated with carbide carbons should be the active site, the atomic-level picture for the carbide surfaces under FTS conditions has long been a mystery, not only because of the pressure gap between the surface characterization techniques (<1 mbar) and FTs operando conditions (10–30 bar) but also because of the great structure similarity among surfaces of different Fe₅C₃ phases.

Recent years have seen encouraging progress regarding probing the surface nature of the as-synthesized Fe₅C₃ catalyst by using transmission electron microscopy (TEM), XPS, and Raman spectroscopy. According to high-resolution TEM, the FT catalyst has a complex core–shell structure with a carbide core and an amorphous carbon layer. Many studies have identified the lattice fringe corresponding to χ-Fe₅C₃(510) with a spacing of ~2.05 Å, suggesting the general presence of χ-Fe₅C₃ in FTS. Other lattice fringes, such as θ-Fe₅C₃(111), χ-Fe₅C₃(100), χ-Fe₅C₃(202), χ-Fe₅C₃(202), χ-Fe₅C₃(311), o-Fe₅C₃(324), and e-Fe₅C₃(101), were detected occasionally, which have the interplanar spacing of 3.02, 2.19, 2.39, 2.65, 2.34, and 2.1 Å, respectively.

By using XPS and Raman spectroscopy, Yang et al. studied the surface of the as-synthesized χ-Fe₅C₃ nanoparticles, which were prepared by using bromide as an inducing agent and Fe(CO)₅ as the precursor reagent. The XPS on the nanoparticle before FTS identified both the Fe₅O₃ phase and the carbide phase on the surface, as shown in Figure 2a: the surface has a C content of 70.55% and an O content of 18.27%. Consistently, the Fe 2p XPS spectrum (Figure 2b) also has two peaks at ~710 and ~724 eV for Fe₅O₃ and two peaks at ~707 and ~720 eV for χ-Fe₅C₃. While their C 1s XPS spectrum (Figure 2c) with a single broad peak at ~285 eV does not distinguish different C species, the Raman spectrum (Figure 2d) exhibits two bands, G-band at 1600 cm⁻¹ and D band at 1328 cm⁻¹, respectively, assigned to the C=C stretching of polyaromatic rings and conjugated olefins, which suggests the existence of (amorphous) graphitic carbon. These graphitic carbon can be reacted off during FTS conditions, as shown by de Smit et al., who studied the evolution of surface carbonaceous species at 1 MPa, 523 K. The G and D bands of graphitic species increase significantly on the catalyst pretreated in low μc (heating to 623 K in 1% CO/H₂) but level off upon reaching 1 MPa on the catalyst pretreated in high μc (heating to 553 K in CO).

Furthermore, de Smit et al. investigated the evolution of C- and O-containing species on the surface of nanoparticle and bulk iron oxide using in situ XPS experiment under 0.3 Torr. The samples were exposed to CO/H₂ (0.1 Torr CO/0.2 Torr H₂) and CO (0.3 Torr) at different temperatures after the reduction of H₂ (0.2 Torr). As shown in Figure 3a,b, they found that both nanoparticle and bulk samples show the increase of total coverage of C- and O-containing species at lower temperatures. When treated in CO/H₂, the nanoparticle mainly grows surface OH species (O 1s 530.8 eV) and carbonates (C 1s 289.8 eV and O 1s 531.9 eV), whereas the bulk sample exhibits a larger contribution of surface oxide (O 1s 531.0 eV) and carboxides (C 1s 283.3 eV, Ccarbide/Fe = 0.07 and 0.04 for bulk and nanoparticle, respectively). When treated in CO, the nanoparticle and bulk samples show a sharp increase of C/Fe ratio above 523 and 573 K, which is attributed to the buildup of Boudouard coke (2CO → CO₂ + C, C 1s 284.6 eV). The nanoparticle sample has a larger content of bulk iron carbide (C 1s 283.3 eV, Ccarbide/Fe = 0.2) and evolves an additional peak at 282.7 eV in the C 1s XPS spectra above 573 K, suggesting the presence of atomic carbon on the surface or in the subsurface. Their results indicate the atomic carbon can form more easily on the surface of nanoparticle iron oxide in reactive gas atmospheres. It should be mentioned that the C 1s XPS spectrum, however, cannot
distinguish different “carbide” with the same coordination pattern, such as those in θ-Fe2C, χ-Fe5C2, and Fe7C3.

Since 2000, a large number of theoretical studies have been performed on the surfaces of FeCx. Although most of them utilized the bulk-truncated surfaces and did not consider the possible surface reconstruction induced by the coverage effect of surface species such as C, H, and CO, some interesting features of FeCx surfaces have been gleaned. For example, Zhao et al. explored the bulk-truncated surfaces of FeC, θ-FeC, χ-FeC, and ε-FeC phases at different μe.27,28 They found that FeC(100), θ-FeC(010), χ-FeC(100), and ε-FeC(121) are the most stable surfaces in each FeC phase, which have the surface free energies of 1.18, 1.60, 1.70, and 1.80 J/m2 at the low μe = −7.20 eV, respectively. These stable surfaces share a very similar surface atom arrangement where each surface C atom coordinates with four surface Fe atoms and each Fe atom coordinates with two C atoms.

By using the SSW-NN method, our group investigated the likely surface reconstruction of FeCx surfaces with different C coverages (variable Fe:C ratio on the surface).51,61 We found that there are 13 surfaces with lower surface free energies, namely, θ-FeC(010), θ-FeC(031), θ-FeC(102), χ-FeC(131), χ-Fe5C2(100), χ-Fe5C2(510), χ-Fe5C2(1(11), χ-Fe5C2(021), χ-Fe5C2(111), ε-FeC(011), ε-FeC(110), and ε-FeC(111). Their surface free energies are 1.50, 1.53, 1.65, 1.78, 1.68, 1.75, 1.81, 1.80, 1.88, 1.79, 1.72, 1.76, and 1.83 J/m2 at μe = −6.90 eV. The FeCx surfaces are dynamic, involving not only structure reconstruction but also the change in composition, which leads to the surface Fe:C ratio being deviated from the bulk Fe:C ratio. Most of these stable surfaces have the same Fe:C ratio of Fe:C = 2 (Fe2C) except χ-Fe5C2(111) (Fe:C = 1.75) and η-FeC(110) (Fe:C = 1.50). These two surfaces with lower Fe:C ratio also have higher Fe−C coordination number, i.e., 2.86 and 3 for χ-Fe5C2(111) and η-FeC(110), respectively, compared to the other 11 surfaces, i.e., θ-FeC(010), θ-FeC(031), θ-FeC(102), θ-FeC(131), χ-Fe5C2(100), χ-Fe5C2(510), χ-Fe5C2(021), χ-Fe5C2(111), ε-FeC(011), and ε-FeC(111), which have the lower Fe−C coordination number of 2, 2.33, 2.67, 2.64, 2.4, 2.7, 2.5, 2.5, and 2.75, respectively. Obviously, most of these low-energy surfaces have the Fe−C coordination number within the range of 2.2−3, suggesting they are the potential active site for FTS according to the experiment by Wang et al.,67 who found that the optimal Fe−C coordination number on the surface could be important for the catalytic performance. The catalyst with too high Fe−C coordination number (>3) produces more undesired CH4, while that with too low Fe−C coordination number (<2.2) turns out to be inactive to FTS.

The adsorption of H and CO have also been examined on low-energy surfaces, which reveals that CO can adsorb generally on the exposed Fe sites of FeCx surfaces. However, H adsorption differs from surface to surface: only eight surfaces, namely, θ-FeC(031), θ-FeC(102), χ-FeC(131), χ-Fe5C2(510), χ-Fe5C2(111), χ-Fe5C2(021), η-FeC(011), and η-FeC(111), that expose at least three adjacent 3-fold Fe sites (except χ-Fe5C2), as shown in Figure 4, can adsorb H atoms exothermically (Gad(H) = −0.18 eV for χ-Fe5C2(111) and −0.40 to −0.30 eV for the other surfaces). They are thus the active site candidates for FTS. It should be noted that θ-FeC(031), χ-Fe5C2(510), and χ-Fe5C2(021) have a similar arrangement (Figure 4) in which the closely linked 3-fold Fe sites are separated by four-coordinated planar C atoms in different ways.

FTS Activity on FeCx. After one century of research, virtually every FeCx detected in experiment has been suggested to be the active phase for FTS.17,18,68,69 Nevertheless, χ-Fe5C2 is perhaps the most accepted active phase as it appears to be the major composition when the high product selectivity to long-chain hydrocarbons is reached in FTS. For example, de Smit et al. found that the catalyst with the higher content of χ-Fe5C2 before FTS (76 ± 5%) has a more stable and higher activity and selectivity to C4+, hydrocarbon chains with time-on-stream, while the catalyst with lower initial content of χ-Fe5C2 (χ-Fe5C2 + θ-FeC, 51%) has a lower selectivity.17 Even more precisely, Yang et al. showed that the as-synthesized single-phase χ-Fe5C2 nanoparticles achieved a 39% initial CO conversion rate and ~59% C5+, hydrocarbon selectivity at the conditions of 543 K
Fe₅C₂ and Fe₂C are the most active phases in terms of initial CO conversion. Fe₅C₂ can maintain the highest CO conversion rate under the conditions of 543 K and 3 MPa. As shown in Figure 5a, Figure 5. (a) CO conversion as a function of time over Fe, Fe₇C₃, Fe₅C₂, and Fe₂C catalysts (543 K, 3 MPa, H₂/CO = 2/1). Reproduced from ref 69. Copyright 2020 Zhao et al. (b) CO conversion and product distribution over RQ Fe catalyst in five successive cycles (443 K, 3 MPa at RT, H₂/CO = 2/1). The recovered catalyst is reused without reactivation. The hydrocarbon selectivities are normalized with the exception of CO₂. Reproduced from ref 57. Copyright 2014 Nature Publishing Group, a division of Macmillan Publishers Limited.

They found that the ε-Fe₂C-dominant RQ_Fe catalyst exhibits superior initial activity for CO conversion to γ-Fe₅C₂-dominant RQ_Fe catalyst by 75% at 443 K and high C₅+ selectivity of 73% at 423 K. They also examined the stability of ε-Fe₂C-dominant RQ_Fe catalyst at 443 K (Figure 5b). The CO conversion decreases by only 4.2%, and the product distributions hardly change from the first run to the fifth run in five successive cycles. This result agrees with the synchrotron XRD pattern of the catalyst after the stability test that ε-Fe₂C remains as the dominant phase. The high stability of the Fe-C catalyst in RQ_Fe compared to that prepared by Zhao et al. may originate from the amorphous (ε-Fe₅C₂(510)),51 the surface observed in the experiment, and found that CO activation via direct dissociation can occur at the surface C vacancies (the barrier is 1.1 eV) that are created dynamically via hydrogenation to CH. The C−C coupling is an important step for producing long-chain products. Although CH₄ coupling reaction, e.g., using CH₂ as the monomer for chain propagation, has been verified on several transition metal surfaces, it remains unclear whether the same mechanism is transferable to FeC₅ surfaces. Until recently, a theoretical study by Yin et al. compared the C₂ formation mechanisms on eight surfaces of γ-Fe₂C₅ and found that the CH₂ coupling is more favorable than CO insertion pathway on all these surfaces, and the C + C coupling on γ-Fe₂C₅(101) is the fastest (the barrier is 1.26 eV) at low H coverage (θH/θC ≈ 10⁻⁵) according to their microkinetics result.

It should be kept in mind that FTS has many elementary steps, including CO activation, C−C couplings, and many hydrogenation reaction steps, including C hydrogenation and O removal. The active sites for different elementary steps may well not be the same, and thus it is important to identify the active sites for the reaction steps that are rate-determining and selectivity-controlling. From previous theoretical studies, the C hydrogenations have relative lower barriers (0.8−1.0 eV), and thus, they should not be the rate-determining step. The O removal steps in H₂O and CO₂ formation appear to have a relative high barrier (1.0−1.5 eV),76,77 and the kinetics of these steps have not been compared systematically with those for CO activation and C−C coupling.

**Outlook.** Through the collective efforts from both experiment and theory, tremendous progress has been made in understanding Fe-based FTS. It is now established that several Fe₅C₂ phases, particularly Fe₅C₂ and Fe₂C, are most likely the active phases based on the thermodynamic stability data and the experimental activity analysis. Although multiple Fe₅C₂ phases coexist, the surfaces of different Fe₅C₂ phases can have identical chemical composition (e.g., Fe:C = 2) and a great similarity in local structure. The catalytic role for other coexisting noncarbide phases, including Fe₅O₈ phases and amorphous and graphitic carbon, although not very clear, appears to be of minor significance. By reviewing the literature, we can outline some
important open issues regarding FeC\textsubscript{x} structures and the reaction mechanism as follows:

(i) The structure of the Fe\textsubscript{2}C\textsubscript{4} bulk phase. Further evidence is required to characterize the \textit{in situ} formed Fe\textsubscript{2}C\textsubscript{4} bulk phase, in particular to distinguish the two O-phases, α-Fe\textsubscript{2}C\textsubscript{4} and α-Fe\textsubscript{2}C\textsubscript{4}-II.

(ii) The junction structure between different FeC\textsubscript{x} phases. Because multiple FeC\textsubscript{x} phases coexist in FTS, the interfaces between them are of significance. If one phase can grow upon another phase readily, the concentration of bulk phase would become less relevant as to the surface active site.

(iii) The structure of FeC\textsubscript{x} surfaces under the FTS condition. To date, most surface-sensitive characterization techniques cannot be operated under the FTS conditions, which limits the deep understanding of the \textit{in situ} surface dynamics. Global neural network-based long-time atomic simulation could be utilized to trace the surface evolution kinetics.

(iv) The O cycle in FTS. After CO activation, the O may end up in several places in FTS, including forming FeO\textsubscript{2} phases, producing CO\textsubscript{2}, H\textsubscript{2}O, and even alcohols. Many unknowns remain to be discovered regarding how the O cycle affects the FTS activity and selectivity.

Obviously, future investigations should be more directed toward real catalyst structures under FTS conditions, which calls for the development of new \textit{in situ} techniques with high spatial and temporal resolution. On the other hand, theoretical studies, especially those based on machine learning techniques, should also play important roles for understanding the active site in Fe-based FTS.

To conclude this Perspective, we mention some emerging fields related to Fe-based catalysts that have generated much new interest in this “old” system:

(i) CO\textsubscript{2} hydrogenation to olefins or long-chain hydrocarbons that is of significance for carbon neutralization.\textsuperscript{78−80} The oxide phases (mainly Fe\textsubscript{3}O\textsubscript{4}) were suggested to play an important role in the reaction, where a CO intermediate is generated from CO\textsubscript{2} via the reverse water gas shift reaction on Fe\textsubscript{3}O\textsubscript{4}.

(ii) The change of FTS selectivity. It is highly desirable to improve the FTS selectivity toward C\textsubscript{5+} products or olefins over the selectivity to C\textsubscript{1−4} products or paraffins. The catalyst modification by doping and restructuring is the focus of new experimental studies. For example, Fe\textsubscript{3}C\textsubscript{4}−Co heterostructured catalyst\textsuperscript{81} and Fe−Zn−Na catalyst\textsuperscript{79,82} were found to increase the selectivity to C\textsubscript{5+} hydrocarbons and olefins. The oxygen-decorated Fe\textsubscript{3}C\textsubscript{4} catalyst under photoirradiation condition\textsuperscript{83} favors the selectivity to lower olefins (C\textsubscript{2−4}). Apart from C\textsubscript{5+} products and olefins, the oxygenate products are additional high-value chemicals being pursued in FTS technology. The Cu−Fe binary catalyst, for example, was shown to produce long-chain alcohols.\textsuperscript{54−56} The catalyst combines the FeC\textsubscript{x} ability toward C−C chain propagation and the Cu activity for CO insertion, the idea of which might be transferable for the design of other catalytic systems.

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\section*{Notes}

The authors declare no competing financial interest.

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