Iron-based Fischer–Tropsch synthesis of lower olefins: The nature of χ-Fe$_5$C$_2$ catalyst and why and how to introduce promoters

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ABSTRACT

As a sustainable and short-flow process, iron-catalyzed direct conversion of CO-rich syngas to lower olefins without intermediate steps, i.e., Fischer–Tropsch-to-Olefins (FTO), has received increasing attention. However, its fundamental understanding is usually limited by the complex crystal phase composition in addition to the interferences of the promoter effects and inevitable catalyst deactivation. Until recently, the combination of multiple in-situ/ex-situ characterizations and theoretical studies has evidenced Hägg iron carbide (χ-Fe$_5$C$_2$) as the dominant active phase of iron-based Fischer–Tropsch catalysts. This perspective attempts to review and discuss some recent progresses on the nature of χ-Fe$_5$C$_2$ catalyst and the crucial effects of promoters on the FTO performance from theoretical and experimental viewpoints, aiming to provide new insights into the rational design of iron-based FTO catalysts.

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1. Introduction

Development of catalysts for direct conversion of CO-rich syngas derived from coal and biomass to lower olefins (C$_2$=–C$_4$=) is of burgeoning scientific and industrial interest [1–4]. Iron catalysts appear to be the best candidate for this purpose, not only because of the lower cost, higher availability, higher selectivity to C$_2$=–C$_4$= and higher resistance to contaminants from a commercial standpoint, but also because of the higher water-gas shift activity to promote the CO reactant reacting with the formed H$_2$O for the generation of H$_2$ in addition to CO$_2$ and thus to enable the in-situ adjustment of H$_2$/CO ratio [5–7]. To steer the product selectivity to light hydrocarbons, the Fischer–Tropsch-to-Olefins (FTO) process is generally carried out at relatively high temperature, which could make full use of the iron-based catalysts with the lower CH$_4$ selectivity compared to other commonly used Fischer–Tropsch catalysts, e.g., Ru and Co [7,8]. Recently, a growing number of studies are conducted to understand the iron-based FTO process with the aim to develop highly efficient iron-based catalysts for the reaction [5–17]. There is an consensus that supported Fe catalysts, especially for using α-Al$_2$O$_3$ and nanostructured carbon materials as the supports, are more suitable for practical applications than unsupported (also referred to as bulk) Fe catalysts, owing to the

higher mechanical stability and dispersion of the active phase [5,7,12,18–20].

The FTO on iron-based catalysts is known to be a structure-sensitive reaction, meaning that the catalytic performance strongly depends on the particle size of the active phase [21–24]. However, limited direct information exists on the effects of the iron particle size on the catalytic performance, mainly because the iron phase composition highly depends on the iron particle sizes, promoters and supports, and the reported catalysts generally undergo deactivation [5,13]. During the pretreatment steps of the iron-based catalysts and real FTO conditions, the carburization process inevitably leads to the formation of a series of metallic Fe, iron carbides (e.g., ε-Fe$_2$C, θ-Fe$_3$C and χ-Fe$_5$C$_2$) and iron oxides (e.g., α-Fe$_2$O$_3$, γ-Fe$_2$O$_3$, Fe$_3$O$_4$ and FeO), significantly increasing the difficulty and complexity in the discrimination of iron active phases [25,26]. Until recently, Hägg iron carbide (χ-Fe$_5$C$_2$) is discriminated as the dominant active phase by the integrated theoretical studies with multiple advanced in-situ/ex-situ characterizations [27].

In this perspective, some recent and theoretical experimental progresses on the nature of χ-Fe$_5$C$_2$ catalyst and the crucial effects of promoters on the FTO performance were reviewed and discussed in detail. Finally, the conclusions and prospects were provided. It is worth noting that for some other critical issues on the fundamentals of the development, application and deactivation of iron-based Fischer–Tropsch catalyst, the readers could refer to several comprehensive reviews [1,25,28,29].

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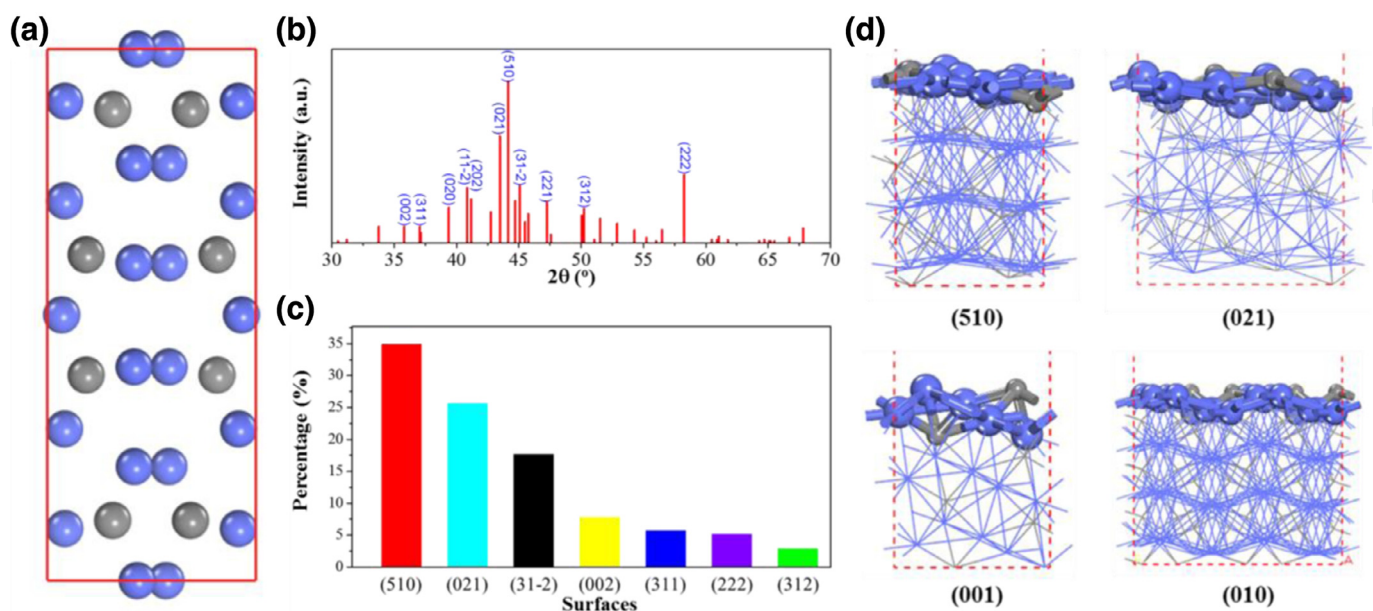[1] These authors contributed equally to this work.

Fig. 1. (a) Geometric structure of the monoclinic (C2/c) unit cell of χ-Fe$_5$C$_2$. (b) Standard XRD pattern of χ-Fe$_5$C$_2$ (JCPDS No. 36-1248). (c) Percentage of the exposed crystal facets of χ-Fe$_5$C$_2$ crystallite on the basis of Wulff construction, where the data originate from Ref. [32]. (d) Side views of χ-Fe$_5$C$_2$ (510), (021), (001) and (010) surfaces, where the blue and gray spheres correspond to the Fe and C atoms, respectively.

2. The nature of χ-Fe$_5$C$_2$ catalyst

2.1. Theoretical studies

χ-Fe$_5$C$_2$ has a monoclinic unit cell with space group C2/c, where the carbon atoms, occupying the interstice between close-packed iron atoms, are located in the trigonal-prismatic interstices (Fig. 1a) [30,31]. Density functional theory (DFT) calculations were carried out to calculate the surface energies of representative 11 facets shown in Fig. 1(b). Fig. 1(c) presents the percentage of the exposed crystal facets of χ-Fe$_5$C$_2$ crystallite based on Wulff construction [32]. It was revealed that some high Miller index surfaces, e.g., χ-Fe$_5$C$_2$ (510) and (021), exhibit lower surface energies and thus are thermodynamically more stable, leading to larger contribution to the total surface area of χ-Fe$_5$C$_2$. These high Miller index surfaces were experimentally observed by HRTEM [30,33–37]. In addition, they are terrace-like, whereas the low Miller index surfaces, e.g., χ-Fe$_5$C$_2$ (010) and (001), are generally step-like (Fig. 1d). These unique features are very different from those of monometallic Fischer–Tropsch catalysts (e.g., Ru, Co and Fe), i.e., the low Miller index surfaces exposed mostly, whilst the high Miller index surfaces being thermodynamically less stable.

There has been an increasing interest on fundamental understanding of the Fischer–Tropsch synthesis mechanism on this unique χ-Fe$_5$C$_2$ catalyst. CO activation is a key step in the initiation of the Fischer–Tropsch synthesis process, and its preferred pathway is used to compare the activity of the catalysts. Generally, the direct CO dissociation pathway corresponds to higher activity in comparison with the H-assisted CO dissociation [38]. Table 1 gives a comparison of the preferred pathways for the CO dissociation among different χ-Fe$_5$C$_2$ surfaces [32,39–43]. Obviously, the direct CO dissociation is the preferred CO activation pathway for the terrace-like χ-Fe$_5$C$_2$ (510) surface, while the H-assisted CO dissociation for the step-like χ-Fe$_5$C$_2$ (010) and (001) surfaces. Additionally, the overall barrier of CO activation on the terrace-like χ-Fe$_5$C$_2$ (510) surface is lower than that on the step-like surfaces. These indicate the terrace-like χ-Fe$_5$C$_2$ (510) surface with higher activity. It could be reasonably deduced that the terrace-like sur-

Table 1. Preferred CO activation pathways of various χ-Fe$_5$C$_2$ surfaces[a].

Surface	Surface characteristics		Preferred CO activation pathways	Ref.
(510)	Terrace-like	Perfect	Direct CO dissociation	[32]
(010)[b]	Step-like	Perfect	H-assisted CO dissociation via HCO intermediate	[39]
		C-vacancy	H-assisted via HCO intermediate and direct CO dissociation	[40]
(001)	Step-like	Perfect	H-assisted CO dissociation via HCO intermediate	[41]
(100)[c]	Step-like	Perfect	Surface carbon hydrogenation[d]	[42,43]
		C-vacancy	H-assisted CO dissociation via HCO intermediate	
		C-free	Direct CO dissociation	

[a] The lattice parameter "a" being higher than the "b" and "c".
[b] χ-Fe$_5$C$_2$ (010)$_{0.25}$ used.
[c] Carbon-terminated χ-Fe$_5$C$_2$ (100)$_{0.05}$ used.
[d] The surface carbon hydrogenation being more active than CO activation.

faces of χ-Fe$_5$C$_2$ act as the active sites for the FTO. This finding is different from the trend for the monometallic Fischer–Tropsch catalysts that the direct CO dissociation prefers to occur at the step sites [44–46]. Moreover, it can be also shown in Table 1 that the presence of C-vacancy on the step-like surfaces facilitates the occurrence of CO dissociation.

In addition to the activity, the product selectivity of χ-Fe$_5$C$_2$ Fischer–Tropsch catalyst is also an important issue for upgrading Fischer–Tropsch products to meet various end-use applications. The pioneering work of Hu and coworkers has used the effective barrier difference between CH$_4$ formation and C$_1$–C$_1$ coupling (ΔE_{eff}) as a descriptor to compare the product selectivity for different Fischer–Tropsch catalysts [47,48]. According to this definition, the higher ΔE_{eff} represents the higher C$_{2+}$ selectivity and the lower CH$_4$ selectivity. Table 2 gives a comparison of ΔE_{eff}