Recent advances in understanding the key catalyst factors for Fischer-Tropsch synthesis

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Abstract
Catalytic conversion of synthesis gas (CO+H₂) into hydrocarbons, also known as Fischer-Tropsch (FT) synthesis, is a crucial reaction for the transformation of non-petroleum carbon resources such as coal, natural gas, shale gas, coal-bed gas and biogas, as well as biomass into liquid fuels and chemicals. Many factors can influence the catalytic behavior of a FT catalyst. This review highlights recent advances in understanding some key catalyst factors, including the chemical state of active phases, the promoters, the size and the microenvironment of active phase, which determine the CO conversion activity and the product selectivity, particularly the selectivity to C⁵⁺ hydrocarbons.

Key words
Fischer-Tropsch synthesis; active phase; catalyst promoter; size effect; microenvironment

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1. Introduction

The depletion of crude oil has stimulated the utilization of non-petroleum carbon resources including coal, natural gas, shale gas, coal-bed gas and biogas, as well as biomass for the production of liquid fuels and chemicals. However, direct transformation of these non-petroleum carbon resources into liquid fuels or valuable chemicals is still highly difficult. One of the most practical ways for the transformation of non-petroleum carbon resources is the production of synthesis gas (syngas, CO+H2) by gasification in the first step, and then, the conversion of syngas into liquid fuels or building-block chemicals in the second step (Figure 1). Typically, two categories of products, i.e., hydrocarbons (e.g., gasoline, diesel and light olefins) and organic oxygenates (e.g., methanol, ethanol and mixed higher alcohols), can be obtained from syngas depending on the catalyst employed for the conversion of syngas.

The transformation of syngas to hydrocarbons, also known as Fischer-Tropsch (FT) synthesis, was first reported by Franz Fischer and Hans Tropsch in 1923 [1]. The main reactions during FT synthesis can be expressed with Equations (1) and (2):

\[(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O\]  

(1)

\[2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O\]  

(2)

The hydrocarbon products can either be liquid fuels such as gasoline, diesel and jet fuel or be building-block chemicals such as lower olefins. The liquid fuels obtained from FT synthesis can be sulphur- and nitrogen-free, and thus may easily meet the increasingly stringent environmental regulations. Some studies have demonstrated that the syngas-based (or FT) fuels are more environmentally friendly than the conventional petroleum-based fuels [2–4]. As a crucial process for the transformation of various non-petroleum carbon resources via the syngas platform, FT synthesis has attracted much renewed interest in recent years because of the diminishing crude oil and the rapidly growing global demand for liquid fuels. From the industrial aspects, in addition to the current FT plants in South Africa (Sasol), Malaysia (Shell) and Qatar (Oryx Sasol), many industrial projects based on FT synthesis have been planned in different countries such as Australia, Bolivia, Chile, China, Egypt, Germany, Indonesia, Iran, Italy, Nigeria, Russia and USA by different companies including Bioliq, BP, EniTechnologie, ExxonMobil, Shenhua, Synfuels China, Synthroleum and Yankuang group [5,6]. Technologies of GTL (gas to liquid), CTL (coal to liquid) and BTL (biomass to liquid) with FT synthesis as a key step have been developed [5–8]. The interest of FT synthesis in academic community has also increased significantly in recent years. The number of publications related to FT synthesis based on ISI Web of Science of Thomas Reuters rose from ~120 in 2000 to ~470 in 2011 (Figure 2).

The catalyst is the key to further improving the efficiency of FT synthesis. The development of FT catalysts with higher activity, selectivity and stability is the main focus of the fundamental research in the field of FT synthesis. There are some excellent reviews on the development of efficient FT catalysts [9–17]. Knowledge has been accumulated for understanding the structure-performance relationships, but some challenges still remain.

FT synthesis follows the polymerization mechanism. It is generally accepted that CO undergoes dissociative or hydrogen-assisted dissociative chemisorption on the surface of Ru, Co or Fe metal or metal carbide nanoparticles, forming CH\(_x\) \((x = 0–3)\) intermediates as the monomers for polymerization [18–22]. The coupling between CH\(_x\) monomers leads to chain growth, providing C\(_n\)H\(_m\) intermediates. C\(_n\)H\(_m\) intermediates with different carbon numbers can then undergo hydrogenation or dehydrogenation to afford paraffins or olefins as the final products. An early work pointed out that the coupling between methylene (CH\(_2\)) groups mainly accounted for the chain growth [23], but recent theoretical studies suggested that the situation was more complicated [24–30]. Depending on the identity and the structure of the surface concerned, the monomeric CH\(_x\) species for polymerization may be different. The calculation of energy barriers suggests that the couplings of (CH+CH), (C+CH), (C+CH\(_2\)) or (CH\(_x\)+HCO) may all be possible [24–30].
The products of FT synthesis follow the Anderson-Schulz-Flory (ASF) distribution because of the polymerization mechanism [31]. According to ASF distribution, ideally, the molar fraction ($M_n$) of the hydrocarbon product with a carbon number of $n$ is only dependent on the chain-growth probability ($\alpha$), which is a function of the rates of chain growth and chain termination, by the following equation:

$$M_n = (1-\alpha)\alpha^{n-1}$$

In other words, the product selectivity is determined by $\alpha$ value in an ideal case. A smaller $\alpha$ value leads to lighter (C$_1$–C$_4$) hydrocarbons, while larger $\alpha$ value results in the formation of heavier (C$_{21+}$) hydrocarbons. However, the ASF distribution is unselective for the middle-distillate products, which are usually the target products. For examples, the maximum selectivity to gasoline-range (C$_5$–C$_{11}$) hydrocarbons is $\sim$45% and that to diesel-range (C$_{10}$–C$_{20}$) hydrocarbons is $\sim$35%. The development of selective FT catalysts, which can tune the selectivities to desired products, is one of the most challenging targets in the field of FT synthesis.

Because of the wide product distribution, FT syncrudes obtained by conventional FT catalysts must be subjected to further refining to produce high-quality liquid fuels such as gasoline, jet fuel and diesel fuel [32,33]. For this purpose, it is necessary to increase the selectivity to C$_5$+ hydrocarbons and to decrease those to CH$_4$ and C$_{2}$–C$_{4}$ paraffins. Most of the publications related to FT synthesis have aimed at developing efficient FT catalysts with high C$_5$+ selectivity as well as high CO conversion activity. On the other hand, as compared with the conventional two-stage process, the direct production of high-quality liquid fuels from syngas without refining stage would be more energy- and cost-efficient, and could increase the competitiveness of FT technology for the production of liquid fuels. This requires the design of novel FT catalysts with high selectivities to a desired range of hydrocarbons [34–41].

The clarification of key factors determining the catalytic behaviors, the development of novel catalysts with enhanced catalytic performances and the elucidation of reaction mechanism were the main targets of fundamental research in FT synthesis in the past decade [9–18]. A large number of studies have pointed out that various factors can influence the catalytic behaviors of a FT catalyst. As summarized in Table 1, besides the engineering factors such as reactor design and operation conditions [5–7,11,42], there exist many catalyst factors, which can exert significant influences on the activity and product selectivity. This short review briefly summarizes some recent studies on clarifying the key catalyst factors for FT synthesis.

### Table 1. Typical key factors influencing the activity and product selectivity of a FT catalyst

<table>
<thead>
<tr>
<th>I. Engineering factors</th>
<th>II. Catalyst factors</th>
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<tbody>
<tr>
<td>(i) Reactor design</td>
<td>(i) identity of active metal (Ru, Co or Fe)</td>
</tr>
<tr>
<td>(ii) Operation conditions</td>
<td>(ii) chemical state of active phase (metal, oxide or carbide)</td>
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<tr>
<td></td>
<td>(iii) support (identity, pore structure, physicochemical properties)</td>
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<tr>
<td></td>
<td>(iv) promoter (typically including noble metals, oxides of Mn, Zr or rare earth metals, alkali metal ions)</td>
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<td></td>
<td>(v) size of active phase</td>
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<td>(vi) microenvironment of active phase</td>
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## 2. Chemical state of active phase

The typical active metals used for FT synthesis are Fe, Co and Ru. The current consensus is that metallic Co and Ru, i.e., Co$^0$ and Ru$^0$ nanoparticles, function as the active phases for CO hydrogenation to heavier hydrocarbons, whereas iron carbides are responsible for CO hydrogenation [15]. However, deeper knowledge about the effects of different chemical states of these active phases on catalytic performances is still needed for the rational design of an efficient FT catalyst.

### 2.1. Co-based catalysts

Metallic Co may exist in two different crystalline forms, i.e., fcc and hcp phases. For bulk Co, the hcp phase is more stable at lower temperatures, but the fcc phase becomes more stable when the size of Co particles becomes less than 20 nm [43]. However, the actual crystalline structure of Co catalyst under working conditions is not well known. Karaca and co-workers recently performed synchrotron-based in situ X-ray diffraction (XRD) studies for a 0.1 wt% Pt-25 wt% Co/Al$_2$O$_3$ catalyst [44,45]. It is found that the supported Co species consisted of $\sim$80% fcc-phase and $\sim$20% hcp-phase in the catalyst after H$_2$ reduction. The size of fcc-phase Co particles increased from $\sim$6 to $\sim$7 nm, whereas the size of hcp-phase Co particles ($\sim$3 nm) did not change during FT synthesis at 493 K under 20 bar of syngas (H$_2$/CO = 2). The reactant atmosphere, however, did not change the ratio of the fcc-phase to hcp-phase Co. With prolonging the time on stream, a significant decrease in CO conversion (from $\sim$60% to $\sim$20%) and a moderate decrease in CH$_4$ selectivity (from $\sim$10% to $\sim$6%) were observed. Co$_2$C was also observed after long-term reactions. The pretreatment of the 0.1 wt% Pt-25 wt% Co/Al$_2$O$_3$ catalyst in pure CO led to the formation of Co$_2$C. After the complete transformation of Co$^0$ to Co$_2$C, the conversion of CO became almost zero. Thus, the formation of Co$_2$C may cause the catalyst deactivation. Another recent work also demonstrated that the deactivation of Co-based catalyst was due to the carbide formation and carbon deposition [46]. Interestingly, the hydrogenation of the supported Co$_2$C caused the preferential formation of hcp-phase Co with an average size of $\sim$9 nm. A detailed comparison revealed that the supported hcp-phase Co showed higher CO conversion activity.
(Co-time yield of the hcp-phase Co was ~1.6 times higher than that of the fcc-phase Co) but a similar product selectivity [45]. The higher activity of the hcp-phase Co was also observed in a study using 0.45 wt% Ru-13 wt% Co/SiO₂ and 13.3 wt% Co/Al₂O₃ catalyst [47]. These observations are consistent with a previous report [48], and further demonstrates that the hcp-phase Co⁰ is more active for CO conversion than the fcc-phase Co⁰. The difference in the product selectivity between the fcc- and hcp-phase Co is, however, insignificant.

Concerning the catalytic behaviors of cobalt carbide (Co₂C) phase in FT synthesis, Karaca and co-workers recently demonstrated that the supported Co₂C was inactive [45]. They also found that Co₂C was stable under the working conditions of FT synthesis if being generated preliminarily with CO [45]. An interesting work reported by Jiao and co-workers showed that the addition of La₂O₃ into a 15 wt% Co/AC increased the selectivity to mixed alcohols (mainly C₂–C₁₈ alcohols) at the expenses of hydrocarbons [49]. For examples, the increase in the content of La₂O₃ from 0 to 0.5 wt% increased the selectivity to mixed alcohols from 22.2% to 38.9% and decreased that of total hydrocarbons from 69.2% to 56.0%. CO conversion rose slightly from 13.5% to 16.9% at the same time. They found that the addition of La₂O₃ promoted the formation of Co₂C in the catalyst after the reaction. It is suggested that the co-existence of fcc-phase Co⁰ and Co₂C is responsible for the higher selectivity to mixed alcohols [49]. However, a recent study using bulk Co₂C synthesized from Co₃O₄ by CO carburization indicated again that Co₂C was less active for FT synthesis, and CO₂ and CH₄ were the main products [50].

In short, recent studies suggest that Co₂C could be formed over some Co-based catalysts during the reaction although the crystalline Co₁₋₂C is a metastable phase under FT reaction conditions. The crystalline Co₂C is inactive for FT synthesis, and the formation of Co₂C may cause the catalyst deactivation. However, the combination of Co⁰ and Co₂C might lead to the formation of mixed alcohols over AC support in the presence of La₂O₃ promoter [49].

### 2.2. Fe-based catalysts

Iron carbides are easily formed under FT reaction conditions because of the lower or similar activation energy for iron carbide formation as compared with that of CO hydrogenation. Many types of iron carbides such as ε-Fe₂C, ε'-Fe₂₋₂C, Fe₇C₃, γ-Fe₃C₂ and θ-Fe₂C all have been observed in FT synthesis [13,15]. However, the true active species under working conditions remains still unsettled. Many studies have been devoted to characterizing the active iron carbide phase. Because the carburized iron catalysts are very sensitive to air exposures even under controlled passivation [52], the in situ or operando characterizations under working conditions are quite important.

De Smit and co-workers performed a series of characterizations on Fe-based catalysts under working conditions [53–55]. By combining in situ scanning transmission X-ray microscopy (STXM) with a nanoreactor, they observed the formation of Fe₁₋₂Si₄O₆ (an Fe⁺⁺ silicate), Fe⁰ and iron carbides (FeₓCᵧ) in a K- and Cu-promoted Fe/SiO₂ catalyst during FT reaction at 523 K under atmospheric pressure of syngas [53]. With in situ X-ray absorption fine structure (XAFS) and wide angle X-ray scattering (WAXS) techniques, it was found that the unsupported Fe catalyst with or without a Cu promoter could be reduced largely to α-Fe in H₂ at 623 K, and the reduced catalysts were easily transformed to θ-Fe₂C under FT conditions (1 bar), but the unsupported Fe catalysts deactivated quite quickly [55]. On the other hand, after the pretreatment with CO/H₂, γ-Fe₃C₅ and fcc-phase γ-Fe co-existed in both the unsupported and the supported Fe catalysts, and these catalysts pretreated by CO/H₂ showed superior activity and stability in FT synthesis [55]. These results suggest that θ-Fe₂C may be responsible for catalyst deactivation, whereas γ-Fe₂C and/or γ-Fe contributed to the stable hydrogenation of CO to heavier hydrocarbons. The same group recently performed comprehensive characterizations on the Fe-based catalyst starting from α-Fe₂O₃ during different pretreatments and under high-pressure (10 bar) reaction conditions by combining experimental techniques including in situ XAFS, XRD and Raman spectroscopy and DFT calculations [55]. As summarized in Table 2, the in situ XRD showed that the starting Fe₂O₃ was converted to γ-Fe₃C₂ phase (~90%) together with a small fraction of ε-carbides (~10%) in pure CO at 553 K, while γ-Fe₃C₂ (~56%) and θ-Fe₂C (~44%) were mainly observed when Fe₂O₃ was pretreated in 1% CO-H₂ gas flow at 623 K. XAFS studies suggested the formation of amorphous iron carbide species (denoted as FeₓC), which could not be clearly seen in XRD, after both pretreatments. Particularly, a larger fraction of FeₓC was observed after the pretreatment in 1% CO-H₂ gas flow at 623 K. After the high-pressure (10 bar) FT reaction at 523 K, the catalyst pretreated in pure CO flow at 553 K underwent some changes, and FeₓO₄ was formed from both XRD and XAFS studies. On the other hand, the catalyst pretreated in 1% CO-H₂ flow did not change significantly during the reaction. The catalyst pretreated in pure CO at 553 K showed higher CO conversion, C₄+ selectivity and CO₂ formation activity, whereas the catalyst pretreated in 1% CO-H₂ gas exhibited lower CO conversion and C₄+ selectivity. Raman spectroscopic studies indicated the buildup of graphitic carbon on the latter catalyst (Table 2), possibly leading to its lower FT catalytic performance. Therefore, θ-Fe₂C and amorphous FeₓC, which possess more metallic nature, are likely to contribute to the higher formation rate of inactive carbonaceous surface species. The result that the catalyst containing FeₓO₄ under working state exhibits a higher CO₂ formation activity suggests that FeₓO₄ is the active phase for the water-gas shift (WGS) reaction.
A recent work was devoted to investigating the Fe species formed in a 13 wt% Fe/SBA-15 catalyst after pretreatments in H2 stream and in syngas stream (H2/CO = 2) and after FT reaction at 703 K using Mössbauer spectroscopy without exposure to air [56]. α-Fe, Fe3O4 and Fe2+ dispersed in the wall of SBA-15 were mainly detected after the pretreatment of the catalyst in H2 stream, whereas χ-Fe5C2, Fe3O4 and Fe3+ dispersed in the wall of SBA-15 were observed in the catalyst after the pretreatment in syngas at the same temperature. After the reaction in syngas for 24 h at 703 K, the catalysts pretreated by both methods were almost the same, mainly comprising Fe3O4, Fe2+ and iron carbides (χ-Fe5C2+ε-Fe22-C). After a long-term reaction (6 days), a higher activity was observed for the catalyst pretreated by H2, and this catalyst showed higher selectivity to light olefins. This was explained by speculating that the iron carbide formed from α-Fe might possess smaller sizes than that directly from Fe2O3, and thus was more active in FT synthesis [56].

Very recently, Yang et al. succeeded in control synthesis of smaller χ-Fe5C2 nanoparticles (∼20 nm) from Fe(CO)5 in the presence of Br− and they found that χ-Fe5C2 nanoparticles with controlled sizes possessed higher catalytic activity for FT synthesis than the catalyst derived from hematite by H2 reduction [57]. Moreover, χ-Fe5C2 nanoparticles showed higher C5+ selectivity than the H2-reduced hematite. The selectivity to lower (C2–C4) olefins, which are key building-block chemicals, accounted for 61% of the whole C2–C4 products and 19% of all carbon products over χ-Fe5C2 nanoparticles without any promoters, whereas the selectivity to C2–C4 olefins was 11% over the catalyst derived from hematite. This further demonstrates that χ-Fe5C2 is an active phase for both CO activation and chain growth. The higher fraction of lower olefins for χ-Fe5C2 also implies the lower hydrogenation ability of the iron carbide phase.

### 3. Promoters

Promoters play important roles in FT synthesis particularly for Fe-based catalysts. Alkali metal ions are known to be essential for suppressing the selectivity to CH4 and enhancing that to C5+ hydrocarbons [5,13,15]. The addition of proper amount of alkali metal ions could also enhance CO conversion and the selectivity to light (C2–C4) olefins [15,58]. However, deep understanding of the nature of the effect of alkali metal promoters is still a challenge.

Many studies suggested that the alkali metal co-adsorbed on model Fe surfaces could increase the heat of CO adsorption possibly owing to the electronic promoting effect [59]. For example, K could weaken the bond of CO adsorbed on Fe, leading to the increase in the dissociation of CO [5,15]. Recently, Huo et al. showed that K promoter could modify the crystallographic orientation in favor of the stabilization of high-index and more active facets through theoretical and experimental studies [60]. Although for clean Fe surfaces, the relative stability decreases in the order of (110) > (100) > (310) > (211) > (210) > (111). DFT calculation suggests that the adsorption of K can change the relative stability of the facets. For example, at K/Fe ratios > 1/48, (211) and (310) become more stable than (100), and a further increase in the K/Fe ratio to 1/12 causes the stabilities of (211) and (310) being even higher than (110). TEM and XRD measurements revealed that the ratios of exposed (211)/(110) and (310)/(110) increased from 69.7/100 and 25.8/100 to 115.2/100 and 73.2/100, respectively [60]. The high-index facets possess step-site lower-coordination Fe atoms. These lower coordination Fe atoms may be more active toward the dissociation of CO, leading to higher CO conversion and C5+ selectivity.

However, it should be noted that metallic iron is not stable under FT reaction conditions. As described in Section 2.2, iron carbides are believed to be the active phase. Thus, it is important to know how the alkali metal ions influence the formation of iron carbides. Ribeiro and co-workers recently reported that the alkali metal ions accelerated the formation of iron carbides through in situ X-ray absorption spectroscopic studies [61]. It is found that the rate of carburization increases in the following order: unpromoted < Li < Na < K = Rb = Cs. The iron species in the catalysts containing 100Fe : 4.6Si : 1.5alkali metal (Li, Na, K, Rb or Cs) were mainly χ-Fe5C2 and Fe3O4 after carburization in CO/He at 563 K for 10 h. It is proposed that the presence of an alkali metal ion with strong basicity (K+, Rb+ or Cs+) increased the dissociative adsorption rate of CO and the surface coverage of the adsorbed CO [61]. This may inhibit the hydrogenation ability and the olefin readsorption ability, contributing to higher C5+ and light olefin selectivities.

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### Table 2. In situ characterization results for Fe-based catalysts (starting from Fe2O3) after different pretreatments and FT synthesis at 523 K under 10 bar of syngas (H2/CO = 1) [55]

<table>
<thead>
<tr>
<th>Status</th>
<th>XRD (vol%)</th>
<th>XAFS (mol%)</th>
<th>Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td>After pretreatment</td>
<td>χ-Fe5C2 (90%)</td>
<td>χ-Fe5C2 (76%)</td>
<td>some graphitic carbon</td>
</tr>
<tr>
<td>After FT synthesis</td>
<td>χ-Fe5C2 (57%)</td>
<td>χ-Fe5C2 (76%)</td>
<td>no significant increase in graphitic carbon</td>
</tr>
<tr>
<td>After pretreatment</td>
<td>χ-Fe5C2 (38%)</td>
<td>Fe5C (14%)</td>
<td>some graphitic carbon</td>
</tr>
<tr>
<td>After FT synthesis</td>
<td>χ-Fe5C2 (56%)</td>
<td>χ-Fe5C2+θ-Fe5C (51%)</td>
<td>some graphitic carbon</td>
</tr>
</tbody>
</table>

a Pretreatment in pure CO flow at 553 K; b Pretreatment in 1% CO-H2 flow at 623 K.
For future studies, it would be quite interesting to gain information about the ratio of iron carbide phase to Fe₃O₄ and the preferentially exposed crystal planes of χ-Fe₅C₂ in the presence and the absence of different alkali metal promoters under working conditions. Furthermore, the investigations of the effects of different facets of iron carbide nanocrystals on the product selectivity and activity would be of high significance.

Manganese is another attractive promoter, because it has been reported that Mn could increase the CO conversion activity and decrease the selectivity to CH₄ for both Fe and Co-based catalysts [5,12,15]. Furthermore, Mn may increase the fraction of olefins in light (C₂–C₄) hydrocarbons [62,63]. The functioning mechanism of Mn is still ambiguous. Recently, Campos and co-workers investigated the effect of Mn added into a Cu-promoted Fe/SiO₂ catalyst by X-ray absorption near-edge structure (XANES) [64]. It was found that Mn substituted for octahedral sites in Fe₃O₄, possibly forming (Fe₁−yMny)₃O₄, and this mixed oxide phase might be responsible for the formation of smaller clusters of Fe₅C, which were more active for CO hydrogenation. However, Ribeiro and co-workers recently reported that Mn did not exert positive effects on product selectivities if the catalyst was pretreated by CO stream before reaction [65]. It was found that the addition of Mn into an Fe-based catalyst hindered the carbonization of Fe species to χ-Fe₅C₂, increasing the fraction of Fe₃O₄ in the pretreated catalyst. The increase in Mn content led to higher CH₄ and C₂–C₄ selectivities, but the selectivity to light olefins decreased. The WGS activity increased due to the increased fraction of Fe₃O₄ in the catalyst. The discrepancy might arise from the support and the catalyst preparation technique. Thus, it should be very careful to employ Mn as a promoter for Fe-based catalysts.

Felts and co-workers reported a significant positive effect of Mn on the product selectivity of a Co/TiO₂ catalyst [66]. They used a preparation technique known as strong electrostatic adsorption (SEA) to introduce Mn species selectively onto Co₃O₄ particles loaded on TiO₂. The addition of Mn significantly decreased the selectivity to CH₄ and increased that to C₅+ hydrocarbons. The ratio of olefins to paraffins in C₂, C₄ and C₆ hydrocarbons also increased with Mn content. Scanning tunnelling electron energy-loss spectroscopy (STEM-EELS) provided clear image of the surrounding of Co₃O₄ particles (~20 nm) by a shell of MnO₂ in the calcined Mn/Co/TiO₂ prepared by SEA technique, whereas MnO₂ was mainly dispersed on TiO₂, separated from Co₃O₄ particles in the catalyst prepared by dry impregnation method [67]. Mn/Co/TiO₂ catalyst prepared by SEA technique exhibited higher C₅+ selectivity than that prepared by dry impregnation. These results allow us to conclude that the enhanced contact between the promoter and the active phase is very crucial. It is noteworthy that the positive roles of Mn in decreasing the selectivity to CH₄ and increasing those to C₅+ hydrocarbons and light olefins have further been confirmed in a recent work using a Mn-promoted Co/SiO₂ catalyst [68].

4. Size of active phase

The size of the active phase is one of the most important factors determining the catalytic behaviors of a heterogeneous catalyst [69]. For Co-based catalysts, Iglesia once analyzed data obtained over different metal oxide-supported Co catalysts, and the results suggested that the turnover frequency (TOF) for CO conversion, i.e., the amount of CO converted per surface Co per time, was independent of the size of Co particles loaded on different metal oxides in a Co-size range of 9–200 nm [9]. The question is whether FT synthesis is a structure-insensitive reaction in the whole Co-size range. Concerning this question, Bezemer and co-workers published an important research work in 2006 [70]. They found that the TOF for CO conversion over carbon nanofiber-supported Co (Co/CNF) catalysts containing Co nanoparticles with mean sizes in a range of 2.6–7 nm increased with Co size up to 6 nm (1 bar) or 8 nm (35 bar) and then remained almost unchanged or only changed slightly with a further increase in Co size. The selectivities to CH₄ and C₅+ hydrocarbons also varied significantly with changing the mean size of Co particles. The selectivity to CH₄ was higher over the catalysts with smaller Co particles, and decreased with increasing Co size particularly in the range of 2.6–8 nm. C₅+ selectivity increased with the mean size of Co nanoparticles monotonically, and the increase became insignificant when Co size exceeded 6–8 nm. Thus, Co-catalyzed FT synthesis is a structure-sensitive reaction in the Co-size range of <10 nm.

Since the work of Bezemer and co-workers, many papers have been published on the Co-size effect in FT synthesis. Some of the results are summarized in Table 3. For example, Xiong and co-workers prepared two series of carbon material-supported Co catalysts, i.e., Co/CNT (CNT = carbon nanotube) and Co/CS (CS = carbon sphere), containing Co particles with mean sizes ranging from 3 to 45 nm, and they found that the TOFs for catalysts prepared using different precursors and different preparation techniques only depended on the size of Co particles [71]. TOFs for both Co/CNT and Co/CS were almost constant when the mean size of Co particles exceeded 10 nm and decreased with a decrease in Co size from 10 to 3 nm. C₅+ selectivity increased with the mean size of Co particles from 3 to 10 nm. Borg et al. found that C₅+ selectivity increased with the size of Co particles from 3 to 7–8 nm over Co/γ-Al₂O₃ catalysts, but they did not observe definite trends in the change of TOF with Co particle size [72]. On the other hand, a recent study for Co/γ-Al₂O₃ with narrowly distributed Co particles sizes showed that TOF increased with Co particle size from 4.8 to 9.3 nm, and then decreased slightly with a further increase in Co particle size [73]. The selectivity to CH₄ decreased and that to C₅+ hydrocarbons increased when Co size was increased from 5.6 to 9.3 nm [73]. The increase in TOF with the size of Co particles was also observed by Prieto and co-workers, who employed ITQ-2, a zeolite with a large external surface area, as the support [74]. When the mean size of Co increased from 5.6 to 10.4 nm, the TOF increased from 1.2×10⁻³ to 8.6×10⁻³ s⁻¹ under reaction conditions of T = 493 K,
\(P = 2.0 \text{ MPa} \) and \( H_2/\text{CO} = 2.64 \). In such a range of Co size, however, the change in product selectivities was insignificant: \( C_5^+ \) selectivity slightly decreased from 68.8\% to 61.6\% with increasing Co size from 5.6 to 10.4 nm [74]. Herranz and co-workers prepared SiO\(_2\)-supported Co nanoparticles with narrow size distribution from colloidal chemistry [75]. They observed the increase in TOF with the size of Co particles from 3.0 to 10 nm.

<table>
<thead>
<tr>
<th>Catalyst (Co size range)</th>
<th>TOF for CO conversion</th>
<th>( C_5^+ ) selectivity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co on metal oxide (9−200 nm)</td>
<td>independent of Co size</td>
<td>increasing with Co-site density</td>
<td>[9]</td>
</tr>
<tr>
<td>Co/CNF (2.6−27 nm)</td>
<td>increasing with Co size up to 6 (1 bar) or 8 nm (35 bar)</td>
<td>increasing with Co size, particularly in the range of 2.6−8 nm</td>
<td>[70]</td>
</tr>
<tr>
<td>Co/CNT and Co/CS (3−45 nm)</td>
<td>increasing with Co size up to 10 nm</td>
<td>increasing with Co size up to 10 nm</td>
<td>[71]</td>
</tr>
<tr>
<td>Co/γ-Al(_2)O(_3) (3−18 nm)</td>
<td>no definite trends</td>
<td>increasing with Co size up to 7−8 nm</td>
<td>[72]</td>
</tr>
<tr>
<td>Co/γ-Al(_2)O(_3) (4.8−17.5 nm)</td>
<td>increasing with Co size up to 9.3 nm</td>
<td>increasing with Co size up to 9.3 nm</td>
<td>[73]</td>
</tr>
<tr>
<td>Co/TTO-2 (5.6−10.4 nm)</td>
<td>increasing with Co size</td>
<td>decreasing slightly with increasing Co size</td>
<td>[74]</td>
</tr>
<tr>
<td>Co/SiO(_2) (2−25 nm)</td>
<td>increasing with Co size up to 10 nm</td>
<td>no information</td>
<td>[75]</td>
</tr>
<tr>
<td>Co/SiO(_2), model catalyst (1.4−10.5 nm)</td>
<td>constant in Co size range of 3.5−10.5 nm and decreasing sharply as Co size decreases from 3.5 to 2.5 nm</td>
<td>CH(_4) selectivity was constant in Co size range of 3.5−10.5 nm and increased on decreasing Co size from 3.5 to 2.5 nm</td>
<td>[76, 77]</td>
</tr>
</tbody>
</table>

Wang and co-workers prepared Co/SiO\(_2\) model catalysts under ultrahigh vacuum (UHV) conditions with various Co coverages (0.25−6.0 ML), corresponding to Co sizes in the range of 1.4−10.5 nm [76,77]. It was found that the catalyst with smaller Co particles (1.4−2.5 nm) exhibited significantly lower TOF and higher CH\(_4\) selectivity than those with larger Co particles (3.5−10 nm). However, both TOF and \( C_5^+ \) selectivity were almost the same when the size of Co particles varied from 3.5−10 nm. Characterizations by XPS suggested that smaller Co particles (1.4−2.5 nm) were oxidized by water vapor during the reaction at 513 K and atmospheric pressure (H\(_2\) : CO : N\(_2\) = 6 : 3 : 1), whereas such oxidation was not evident for larger Co particles (3.5−10.5 nm). Therefore, Wang and co-workers proposed that the Co-catalyzed FT synthesis was intrinsically structure-insensitive because of the lack of intrinsic particle size effect for Co\(^0\) particles in the range of 3.5−10.5 nm [76,77].

In short, except for the work reported by Wang and co-workers [76,77], most of recent studies have demonstrated similar Co particle size effects to those reported by Bezenner and co-workers; TOF increases with Co particle size to a critical point and then changes slightly (Figure 3). With respect to the product selectivity, the observed general trend is that the selectivity to CH\(_4\) decreases and that to \( C_5^+ \) hydrocarbons increases with increasing Co particle size (Figure 3). It is noteworthy that the fraction of olefins in the hydrocarbon products has also been found to be Co-size dependent in several studies. For example, Park et al. observed that larger Co particle size led to higher fraction of olefins in C\(_2\)−C\(_4\) hydrocarbons [73]. Borg et al. found a positive correlation between \( C_5^+ \) selectivity and the olefin/paraffin ratio [72]. The higher olefin/paraffin ratio may reflect lower hydrogenation ability of larger Co particles, resulting in relatively higher chain growth probability and higher \( C_5^+ \) selectivity.

Size effect studies for Ru- and Fe-based catalysts are not numerous. A few early studies pointed out the increase in TOF for CO hydrogenation with increasing the size of Ru or Fe particles (or decreasing the metal dispersion) [78−80]. It was also showed that the TOFs over Ru catalysts loaded on metal oxides such as SiO\(_2\), Al\(_2\)O\(_3\) and TiO\(_2\) were independent of the dispersion of Ru in a range of 0.0009−0.60 [81]. Recently, Xiao and co-workers found that Ru nanoclusters stabilized by poly(N-vinyl-2-pyrrolidone) (PVP) which were highly dispersed in water, could catalyze FT synthesis in aqueous phase under 2 MPa H\(_2\) and 1 MPa CO at 423 K [82]. Ru nanoclusters with a size of 2 nm exhibited the highest TOF for CO conversion (∼3.6×10\(^{-3}\) s\(^{-1}\) at 423 K), while significant lower TOFs were observed with too smaller or too bigger PVP-stabilized Ru nanoclusters dispersed in H\(_2\)O. The absence of support may allow us to gain more straightforward information about the Ru particle size effect, but the PVP covering on the surface of Ru nanoclusters may rather increase the complexity. Carballo et al. investigated the size effect of Ru particles loaded on γ-Al\(_2\)O\(_3\), and found that FT synthesis with Ru/γ-Al\(_2\)O\(_3\) was a strong structure-sensitive reaction when the size of Ru particles was smaller than 10 nm [83]. The TOF for CO conversion at 523 K under 5.5 kPa CO and 55 kPa H\(_2\) increased from 0.029 s\(^{-1}\) to 0.129 s\(^{-1}\) with increasing the size of Ru particles from 4 to 12 nm, and then changed...
only slightly. CH\textsubscript{4} was formed as a main product because of the high H\textsubscript{2}/CO ratio (10/1) employed in this study. We have performed size-effect studies for FT synthesis catalyzed by Ru nanoparticles loaded on CNTs [35]. The TOF increased significantly with increasing the mean size of Ru particles from 2.3 to 6.3 nm, and a further increase in the mean size of Ru slightly decreased the TOF. \( C_{5+} \) selectivity over Ru/CNT catalysts underwent gradual increases with increasing the mean size of Ru particles from 2.3 to 6.3 nm. 

Park et al. reported a study on Fe particle size effect [84]. They prepared Fe\textsubscript{6}/Al\textsubscript{2}O\textsubscript{3} catalyst from pre-synthesized \( \gamma \)-Fe\textsubscript{2}O\textsubscript{3} with particle sizes varying from 2–12 nm. After reduction in H\textsubscript{2} at 723 K, the sizes of Fe\textsuperscript{0} particles in these catalysts were evaluated to be 2.4–11.5 nm by CO chemisorption. The analyses of the FT reaction results at 553 and 573 K for the catalysts with different Fe\textsuperscript{0} particle sizes showed that the TOF increased from 0.06 to 0.187 s\textsuperscript{-1} with increasing the size of Fe particles from 2.4 to 6.2 nm, and then it kept almost unchanged with a further increase in Fe size to 12 nm. The selectivities to CH\textsubscript{4} and C\textsubscript{2}–C\textsubscript{4} decreased and that to C\textsubscript{5+} hydrocarbons increased monotonically with increasing the size of Fe nanoparticles. Sun et al. recently prepared Fe\textsubscript{2}O\textsubscript{3} nanoparticles with mean sizes ranging from 8.3 to 22 nm highly dispersed over mesoporous carbon materials and exploited these Fe-containing mesoporous carbon materials as catalysts for FT synthesis [85]. It was found that CO conversion gradually decreased with increasing the size of iron particles. However, CO conversions used for size-effect discussion were too high to evaluate the intrinsic reaction rate, i.e., TOF. The selectivity to CH\textsubscript{4} decreased and that to C\textsubscript{5+} hydrocarbons increased with decreasing the size of Fe particles from 22 to 8.3 nm. C\textsubscript{5+} selectivity reached \( \approx \)60% over the catalyst with a mean size of Fe particles of 8.3 nm, and this was an excellent C\textsubscript{5+} selectivity by considering the absence of alkali promoters. The trend of the variation of selectivity with Fe particle size is, however, different from that observed by Park et al. [84]. The integral reaction conditions (higher CO conversions) used in this work [85] may complicate the trend because a variety of secondary reactions may occur under these conditions.

It should be noted that Fe\textsuperscript{0} nanoparticles are typically transformed into iron carbide species during FT synthesis. Thus, the evaluation of size of iron carbide species is important. A very recent study using Fe carbide (\( \chi \)-Fe\textsubscript{5}C\textsubscript{2}) nanoparticles with different sizes loaded on CNFs revealed that the TOF for CH\textsubscript{4} formation increased sharply on decreasing the size of Fe carbide particles from 4 to 2 nm, whereas the TOF for C\textsubscript{2+} hydrocarbon formation was almost independent of Fe carbide particle size [86]. These trends are quite different from those observed for Co- and Ru-based catalysts (Figure 3). Further studies revealed that lower olefins may be produced at promoted terrace sites, while CH\textsubscript{4} might be formed at highly active low-coordination sites residing at corners and edges of \( \chi \)-Fe\textsubscript{5}C\textsubscript{2} [86].

It is generally accepted that the activation of molecules with \( \pi \)-bonds such as CO or N\textsubscript{2} requires a reaction centre with a unique configuration of several metal atoms and step-edge sites, which may not be present on smaller metal particles [87]. Thus, the TOF may increase with increasing the size of metal particles, and this has been classified as class-I structure sensitivity [69,87]. Actually, the TOF for NH\textsubscript{3} synthesis increases with the sizes of Fe and Ru particles [88,89]. FT synthesis is a more complicated reaction, comprising many elementary steps such as dissociative adsorption of CO as well as H\textsubscript{2}, hydrogenation of adsorbed C to form CH\textsubscript{x} species, coupling of CH\textsubscript{x} to C\textsubscript{n}H\textsubscript{m} intermediates and the formation of products (mainly paraffins and olefins) from C\textsubscript{n}H\textsubscript{m} intermediates via hydrogenation or dehydrogenation. It can be expected that the combination of different sites may be required for the formation of final products. This may lead to higher TOF for CO conversion and higher C\textsubscript{5+} selectivity over larger Co, or Ru particles.

By steady-state isotopic transient kinetic analysis (SSITKA) technique, the groups of de Jong and Holmen performed studies on the surface coverages and residence times of different intermediates on Co/CNF and Co/\( \gamma \)-Al\textsubscript{2}O\textsubscript{3} catalysts with different mean sizes of Co particles [90,91]. The results suggested that very strongly bonded carbon and oxygen surface species or irreversibly bonded CO species increased with decreasing the size of Co particles, and these species might act as the site-blocking species, leading to lower TOF for smaller Co particles (<6 nm). Herranz and co-workers clarified through H-D exchange experiments that the rate of H\textsubscript{2} dissociation was lower over smaller Co particles than that over larger ones, leading to lower hydrogenation TOF for smaller Co particles [75]. Actually, during FT synthesis, the surface coverage of CH\textsubscript{x} species, which should be responsible for the formation of hydrocarbons, was found to be lower over the catalysts with smaller Co particles [90,91]. These may lead to both lower TOF and lower C\textsubscript{5+} selectivity for smaller Co particles.

5. Microenvironment of active phase

The location or the microenvironment of active phase in the catalyst has been found to exert significant influences on the activity and selectivity in FT synthesis. Particularly, the confinement of active phases in a nanospace may change the catalytic behaviors, mainly selectivity, by the shape selectivity, diffusion control or enhanced re-adsorption of \( \alpha \)-olefin intermediates. The confinement may also limit the growth of active phases, i.e., Ru, Co or iron carbide nanoparticles, during FT synthesis. Recently, the sintering of metal nanoparticles has been confirmed to be one of the main reasons for the deactivation of Co-based catalysts [92].

Early studies demonstrated that the encapsulating of metal nanoclusters in the supercage of faujasite zeolites affected their catalytic performances in FT synthesis [93–95]. Recently, Xiong and co-workers compared the catalytic performances of Ru nanoparticles confined in the mesoporous channels of SBA-15 (denoted as Ru-in-SBA-15) and those located outside the mesopores of SBA-15 (denoted as Ru-out-SBA-15), and they found that the confined Ru nanoparticles exhibited significantly higher C\textsubscript{5+} and lower CH\textsubscript{4} selectivities than the Ru particles located outside the mesopores although
the CO conversion activity was lower (Table 4) [96]. It is proposed that the confinement may enhance the repeated re-
adsorption of \( \alpha \)-olefin intermediates, leading to higher \( C_{5+} \) selectivity.

Table 4. Effect of microenvironment of active phases on CO conversion (or activity) and product selectivity in FT synthesis

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>CO conversion (% or activity)</th>
<th>Selectivity (%)</th>
<th>Mean particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO(_2)</td>
<td>CH(_4)</td>
<td>C(_2)-C(_4)</td>
</tr>
<tr>
<td>Ru-in-SBA-15(^a)</td>
<td>37 mmol·h(^{-1})·g(^{-1})</td>
<td>n.a.(^b)</td>
<td>23</td>
</tr>
<tr>
<td>Ru-out-SBA-15(^b)</td>
<td>50 mmol·h(^{-1})·g(^{-1})</td>
<td>n.a.(^b)</td>
<td>39</td>
</tr>
<tr>
<td>Fe/AC(^c)</td>
<td>17%</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>Fe-in-CNT(^d)</td>
<td>40%</td>
<td>18</td>
<td>12</td>
</tr>
<tr>
<td>Fe-out-CNT(^d)</td>
<td>29%</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Fe-in-CNT(^d)</td>
<td>85%</td>
<td>39</td>
<td>26</td>
</tr>
<tr>
<td>Fe-out-CNT(^d)</td>
<td>79%</td>
<td>40</td>
<td>41</td>
</tr>
<tr>
<td>FeN-in-CNT(^f)</td>
<td>0.93 mmol·s(^{-1})·g(_{Fe})(^{-1})</td>
<td>39(^g)</td>
<td>27</td>
</tr>
<tr>
<td>FeN-out-CNT(^f)</td>
<td>0.61 mmol·s(^{-1})·g(_{Fe})(^{-1})</td>
<td>35(^g)</td>
<td>32</td>
</tr>
<tr>
<td>Fe-in-CNT(^f)</td>
<td>0.13 mmol·s(^{-1})·g(_{Fe})(^{-1})</td>
<td>22(^g)</td>
<td>31</td>
</tr>
<tr>
<td>Fe@C sphere(^g)</td>
<td>2.5 L·h(^{-1})·g(_{Fe})(^{-1})</td>
<td>23(^g)</td>
<td>14</td>
</tr>
<tr>
<td>Fe/SiO(_2)(^h)</td>
<td>1.6 L·h(^{-1})·g(_{Fe})(^{-1})</td>
<td>20(^g)</td>
<td>n.a.(^b)</td>
</tr>
</tbody>
</table>

\(^a\) From Ref. [96]: Ru loading, \( \sim 4 \) wt\%, \( T = 508 \) K, \( P = 1 \) MPa, H\(_2\)/CO = 2/1; \(^b\) Not available; \(^c\) From Ref. [102]: Fe loading, 10 wt\%; \( P = 5.1 \) MPa, \( H_2/CO = 2; \(^d\) From Ref. [103]: Fe loading, 12 wt\%, \( T = 543 \) K, \( P = 2 \) MPa, \( H_2/CO = 2; \(^e\) \( CO \) selectivity was calculated separately from the hydrocarbon selectivity; \(^f\) From Ref. [105]: Fe loading, \( \sim 5–6 \) wt\%, \( T = 573 \) K, \( P = 5 \) bar, \( H_2/CO = 1/1; \(^g\) From Ref. [107]: \( T = 543 \) K, \( P = 2 \) MPa, \( H_2/CO = 2 \); \(^h\) From Ref. [108]: Fe loading, \( \sim 7 \) wt\%, \( T = 543 \) K, \( P = 2 \) MPa, \( H_2/CO = 2 \).

CNTs may provide an intriguing confinement environment for metal nanoparticle catalysts, and some studies have demonstrated that the confinement of active phases inside CNTs can bring about positive effects in different catalytic reactions [97–99]. Chan et al. successfully prepared Fe\(_2\)O\(_3\) clusters inside and outside CNTs with similar sizes, and they found that the confined Fe\(_2\)O\(_3\) particles were reduced more easily [100,101]. The catalytic studies showed that, as compared with Fe catalyst outside the CNTs (Fe-out-CNT), Fe catalyst inside CNTs (Fe-in-CNT) exhibited both higher CO conversion and higher \( C_{4+} \) selectivity, while the selectivities to CH\(_4\) and \( C_2\)–\( C_4 \) hydrocarbons were lower over Fe-in-CNT catalyst (Table 4) [102]. \( C_{5+} \) yield over Fe-in-CNT catalyst was about twice higher than that over Fe-out-CNT catalyst. Abbaslou and co-workers also studied Fe catalysts located mainly inside and outside CNTs for FT synthesis, and observed similar superiority of Fe-in-CNT catalyst for the formation of \( C_{4+} \) hydrocarbons (Table 4) [103]. They found that the sizes of iron kept almost unchanged in Fe-in-CNT catalyst, while they increased significantly from \( 5–9 \) nm to \( 6–24 \) nm in Fe-out-CNT catalyst. In situ XRD characterizations revealed that a larger fraction of iron carbide was formed over Fe-in-CNT catalyst [102]. The ratio of the intensities of diffraction peaks belonging to iron carbide and Fe\(_2\)O\(_4\), denoted as \( I(Fe_2C)/I(Fe_2O_4) \), was \( \sim 4.5 \) for Fe-in-CNT after the steady-state was achieved, whereas it was smaller than \( 2.5 \) for Fe-out-CNT catalyst at steady state [102]. In short, as compared with Fe species located outside the CNTs, Fe species inside the CNTs demonstrate superior CO conversion activity and \( C_{3+} \) selectivity. The following advantages can be expected for Fe species inside CNTs: (1) higher fraction of iron carbide species; (2) less coalescence of iron species under reaction conditions; (3) possible enhanced re-adsorption of \( \alpha \)-olefins. Furthermore, Guan et al. recently showed that CO was more enriched than H\(_2\) inside CNTs because of the stronger interaction of CO with the CNT interior surface, resulting in a higher CO/H\(_2\) ratio inside the CNTs [104]. This may also contribute to the increase in the selectivity to \( C_{5+} \) hydrocarbons.

Recently, Guan et al. succeeded in preparing cubic Fe\(_2\)N nanoparticles confined in CNTs (denoted as Fe\(_2\)N-in-CNT), and they found that the confined Fe\(_2\)N nanoparticles were more active for FT synthesis [105]. Such an Fe\(_2\)N catalyst exhibited a \( 5–7 \) times higher activity than a reduced Fe catalyst and an Fe\(_2\)N/\( \gamma \)Fe\(_2\)O\(_3\) catalyst. Fe\(_2\)N-in-CNT catalyst was also more active than Fe-in-CNT and Fe\(_2\)N-out-CNT catalyst (Table 4), indicating that Fe\(_2\)N was a more efficient phase for CO hydrogenation and the positive effect of the confinement. Fe\(_2\)N was transformed to Fe\(_2\)C\(_x\)N\(_{1−x}\), Fe\(_2\)C\(_x\)N\(_{1−x}\) and \( \gamma \)-Fe\(_2\)N during FT reaction for both Fe\(_2\)N-in-CNT and Fe\(_2\)N-out-CNT catalysts, and almost no Fe\(_2\)O\(_4\) was observed. The surface carbon formed from the dissociative adsorbed CO may diffuse into the lattice of Fe\(_2\)N and replace a part of nitrogen atoms. A higher fraction of Fe\(_2\)C\(_x\)N\(_{1−x}\) was observed in Fe\(_2\)N-in-CNT catalyst. The confinement may have a strong retention of nitrogen in the lattice. Both Fe\(_2\)N-in-CNT and Fe\(_2\)N-out-CNT catalysts exhibited higher WGS activity and higher selectivity to \( C_2\)–\( C_4 \) hydrocarbons (Table 4). The ratio of olefins to paraffins in \( C_2\)–\( C_4 \) was \( 2.6–3.0 \), indicating that these Fe\(_2\)N-based catalysts may be used for the production of light olefins. The addition of \( 0.5–2.0 \) wt\% Mn into Fe\(_2\)N-in-CNT catalyst further increased the ratio of olefins to paraffins in \( C_2\)–\( C_4 \) to \( 5.3–5.6 \), providing a \( C_2\)–\( C_4 \) olefin selectivity of \( \sim 44\% \) [106].

Yu and co-workers synthesized carbonaceous spheres embedded with highly dispersed iron oxides nanoparticles (denoted as Fe@C sphere) by a hydrothermal cohydrolysis-carbonization process using glucose and iron nitrate as starting materials [107]. After reduction in H\(_2\) at 673 K, the C sphere possessed a size of \( \sim 5 \) \( \mu \)m, and the particle size of iron species inside the C sphere was \( \sim 7 \) nm. Iron oxides were

\[ \text{Fe}_n\text{O}_m \]
transformed to iron carbides, mainly $\theta$-$\text{Fe}_2\text{C}$ and $\chi$-$\text{Fe}_3\text{C}_2$. There existed mesopores inside the C sphere, ensuring the accessibility of the embedded iron species to syngas. This catalyst was quite stable during the reaction because of the confinement of Fe species inside the C sphere. Furthermore, because the iron species were surrounded by carbon in the catalyst, the fraction of iron carbides reached 88% in the reduced catalyst, which caused higher activity of this catalyst than other supported Fe catalysts such as Fe/SiO$_2$ (Table 4). The Fe@C sphere also showed a higher C$_5^+$ selectivity (60%) than most of the Fe-based catalysts.

6. Concluding remarks

Fischer-Tropsch synthesis has received much renewed interest in recent years because it is a crucial reaction for the transformation of various non-petroleum carbon resources such as coal, methane and biomass into liquid fuels or chemicals via syngas. Many recent studies have shed light on the key factors determining the catalytic behaviors of FT catalysts. The rate (TOF) of CO conversion and the selectivity to C$_5^+$ hydrocarbons are the main concerns of most studies. As far as the catalyst factors are concerned, the chemical state of active phases, the presence of suitable promoters, the size and the microenvironment of active phases play pivotal roles. For Co-based catalysts, recent studies suggest that hcp-phase Co is more active than the fcc-phase Co, whereas Co$_2$C is inactive for FT synthesis. Through extensive characterization studies, it becomes clear that $\chi$-$\text{Fe}_3\text{C}_2$ is the active phase for Fe-based catalysts. The controlled synthesis of small $\chi$-$\text{Fe}_3\text{C}_2$ nanoparticles has provided both higher activity and higher C$_5^+$ selectivity than the conventional Fe catalysts derived from hematite by H$_2$ reduction. Promoters play important roles particularly in Fe- and Co-based catalysts. The roles of some typical promoters such as alkali metal ions and MnO$_x$ are still in debate. Deeper studies on the function of promoters in well-defined catalysts on molecular scale are still lacking. On the other hand, significant advances have been made in elucidating the effect of size of active phase. Most of the studies on size effects have pointed out that FT synthesis is a structure-sensitive reaction. The results obtained for many Co- and Ru-based catalysts all indicate that the TOF for CO conversion increases with the size of metal nanoparticles up to a critical point (6–10 nm) and then changes slightly. For Fe-based catalysts, the results are still inconsistent. The confinement of active phase inside CNTs or other nanospaces has some distinct advantages in improving the activity, C$_5^+$ selectivity and stability. Future studies are needed to provide deeper understanding of the function of promoters, the nature of size effects and confinement effects.

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