1. Introduction

Fischer-Tropsch (F-T) synthesis remains the core technology for producing non-petroleum-based fuels. The product selectivity of F-T synthesis has been restricted by the Anderson-Schulz-Flory (ASF) distribution. New designs of F-T catalysts and reaction pathways that can break these selectivity limitations are extremely important. Notable developments in F-T applications for producing unconventional F-T products such as light olefins (C2-C4), gasoline (C5-C11), jet fuel (C8-C16) and oxygenated organic compounds have been made. Synthesis of these high-value hydrocarbons demands the design of new F-T catalysts that can effectively tune the product distribution beyond the limits of the ASF distribution. Several reaction pathways and high-efficiency F-T catalysts with exceptional catalytic performances have been proposed. This review describes significant advances in terms of rational design of catalysts, particularly for the F-T synthesis of high-demand hydrocarbons. Our perspectives regarding the key factors for enhancing catalytic performances are discussed to open new approaches for future projects.

Keywords
F-T synthesis, Gasoline, Jet fuel, Light olefin, Oxygenated organic compound

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Co-based catalysts generally exhibit high selectivity for linear long-chain hydrocarbons and low WGS reaction activity\(^{9,10}\). Ru-based catalysts are the most active but the most expensive, which limits large-scale industrial application. Modification of the properties of these F-T catalysts, including particle size, metal particle dispersion, crystalline phases, additives, promoters, support material and others, reaction parameters and reactor design may influence the product distribution\(^{3,11,12}\), reduce selectivity for undesirable products (such as methane) and optimize the selectivity for heavy (C\(^{5+}\)) hydrocarbons\(^6\). Nonetheless, single-pass conversion of syngas into a specific range of C\(^{2+}\) hydrocarbons, with tunable selectivity, remains one of the key challenges in F-T technology.

Presently, conventional F-T products are further passed through refining processes such as hydro-treatment for improvement of desired liquid fuel selectivity. Compared to the existing energy-intensive multi-step process, the direct production of a specific range of liquid fuels would be more energy efficient, and more economical. Therefore, new catalyst design strategies and reaction pathways are very important to improve the ASF distribution.

C\(^{2+}\) hydrocarbons (light olefins, gasoline, jet fuel and oxygenates) are primarily produced from petroleum. However, due to recent advances in F-T catalyst design, these liquid fuels and high-value chemicals can now be directly synthesized via F-T synthesis. This review focuses on these new developments based on F-T synthesis and highlights possible future directions.

### 2. Light Olefins (C\(^{2+}\)-C\(^{4}\)) Direct Synthesis via F-T Synthesis

Light olefins (ethylene, propylene and butene) are essential building-block chemicals widely used in the plastics, pharmaceutical and cosmetics industries. C\(^{2+}\)-C\(^{4}\) olefins are mainly produced at petroleum refineries by the FCC process\(^{13}\). In general, Fe-based catalysts have higher olefin to methane selectivity, compared to Co or Ru-based catalysts in the Fischer-Tropsch to Olefins (FTO) process.

Strategies to control the reaction path by modifying conventional Fe-based catalysts are constantly under investigation to tune the product selectivity to avoid the ASF constraint. Our group developed an (Fe/SiO\(_{2}\)) core (Silicalite-1 membrane) shell structured catalyst in 2011, using the secondary growth method, as shown in Fig. 1\(^{11}\). The Silicalite-1 zeolite shell was essential in the optimization and regulation of product distribution. Compared to the naked Fe/SiO\(_{2}\) catalyst, the zeolite shell tightly enclosed the core catalyst (Fe/SiO\(_{2}\)-S), resulting in a confined reaction environment and shape selectivity effect in the FTO reaction which regulated the F-T reaction equilibrium and enhanced the selectivity for light alkenes. The ratio of olefins to paraffins was 0.46 for the Fe/SiO\(_{2}\)-S capsule catalyst at 380 °C, 1.0 MPa and CO/H\(_{2}\) ratio of 1/2, compared to 0.37 for the naked Fe/SiO\(_{2}\) catalyst. Simultaneously, formation of undesired long-chain hydrocarbons over the zeolite capsule catalyst was reduced to 35.2%. The sieving effect of the Silicalite-1 shell increased the diffusion rates of smaller molecular size hydrocarbons and prohibited the re-adsorption of light alkenes resulting in reduction of extended C-C chain propagation. The zeolite (Silicalite-1) shell of the Fe/SiO\(_{2}\)-S capsule catalyst also controlled the concentration of CO in the core catalyst region by reducing the CO diffusion rate resulting in increased local H\(_{2}/\)CO ratio, which probably influenced the observed decrease in selectivity for heavy hydrocarbons.

Iron-based (Fe-Zr) catalysts were successfully modified by a promoter (Zn) using microwave-hydrothermal and impregnation methods, and applied for synthesis of light olefins via the F-T route\(^{13}\). The addition of a Zn promoter using an appropriate method optimized the chemical environment of the Fe, and enhanced both the...
light olefin selectivity and catalyst stability. Zn is well-known to have hydrogen activation abilities, so increased activated hydrogen would enhance reduction of the Fe species. X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) characterizations clearly revealed that the catalyst prepared by the impregnation approach (Zn20, where 20 = wt%) had larger particle sizes with greater quantities of surface ZnO, resulting in severe carbon deposition. However, the Zn20M catalyst was synthesized via the one-step microwave-hydrothermal method with well-dispersed Zn and Fe phases, so that many more active Fe sites were accessible for FTO synthesis, resulting in superior CO conversion (95.9 %) and improved stability (200 h). Additionally, the Zn20M catalyst had enhanced surface area and greater pore volume compared with the Zn20 catalyst. Therefore, the Zn20M catalyst probably had better mass transfer and diffusion activities of reactants and products, resulting in the increase in light olefin selectivity from 38.1 to 40.9 %. Additionally, strong interactions between Fe and Zn species probably attenuated chain growth and secondary hydrogenation of the light olefin products. Further increase (> 20 wt%) in the Zn content resulted in lower BET surface areas and pore volumes, which led to high CH₄ selectivity. Therefore, Zn promoters enhanced light olefin selectivity in Fe-based catalysts, but the efficiency strictly relied on the quantity and method of catalyst preparation.

Highly active F-T (Fe/NMCs) catalysts with high iron (40 wt%) content loaded over nitrogen-rich mesoporous carbons (NMCs) were prepared using the incipient wetness impregnation method. These Fe/NMCs catalysts displayed remarkable productivity of light olefins (0.62 g HC/(h g cat.), higher than that of any other reported iron catalyst under the reaction conditions of 260 °C, 1 MPa and H₂/CO ratio = 1. The mesoporous carbon support had unique properties, with high porosity and large surface area which enabled both high metal loading and improved metal dispersion, thus exposing more active Fe sites for accelerated CO activation resulting in enhanced catalytic activity. The tuned nitrogen content provided anchoring sites (N-groups: pyrrolic N and pyridinic N) for the Fe atoms which significantly enhanced the dispersion of iron as shown in Fig. 2. The unique interaction of the Fe metal with the support enhanced the catalytic performance, demonstrating NMCs as the ideal support for iron-based F-T catalysts. Furthermore, the strong basicity of the nitrogen-containing groups resulted in significant decrease in the methane selectivity, thus improving the selectivity for light olefins. Therefore, nitrogen containing groups can be effectively used as metal binding sites to improve metal dispersion and also to increase surface basicity for better light olefins selectivity.

A series of Fe-based (Fe/rGO) reduced graphene oxide (rGO) catalysts were prepared with various amounts of Mn loaded onto the Fe/rGO via ultrasonic assisted impregnation, resulting in Mn-rich shells of Mn and Fe mixed oxides encapsulating Fe-rich cores, as shown by the XRD, transmission electron microscope (TEM), and XPS characterizations. These
catalysts (Fe-Mn/rGO) were tested against Mn-free Fe/rGO catalysts in a slurry bed reactor. Under the optimum reaction conditions of 2 MPa, 300 °C, 4.2 L g⁻¹ h⁻¹ and syngas (H2/CO) ratio = 1, the FeMn16 (Mn loading up to 16/100 mol Fe) catalyst achieved the highest olefin yield of 19 % at an O/P ratio of 0.7. The Mn migration tendencies which resulted from the weak interaction between Mn and the rGO support caused higher surface basicity. Strong basicity is generally positively correlated with olefins selectivity. The Mn shell successfully tuned the gas absorption preferences by increasing the dissociative adsorption of CO and decreasing H2 adsorption, so increasing CO conversion (up to 84 %) and reducing hydrogenation activities, resulting in improved olefins selectivity. Doping of an appropriate amount of Mn also assisted in stabilizing the active Fe-C phase. Nonetheless, excessively thick Mn shells shielded the active sites and reduced diffusion efficiency of the reactants to the catalyst core resulting in lower catalytic performance. Therefore, the optimum shell thickness is required for improved catalytic performance.

3. Gasoline (C5-C11) Range Hydrocarbons Direct Synthesis via F-T Synthesis

Efficient utilization of the active catalyst sites and simultaneous enhancement of target hydrocarbon selectivity in Fischer-Tropsch synthesis (F-T) of syngas direct synthesis of isoparaffins were achieved by direct hydrothermal crystallization of a compact, central zeolite shell H-ZSM-5 on the exterior of fused-iron catalyst pellets. The as-synthesized catalyst had a core-shell structure without cracks and pinholes, and completely suppressed the formation of C10+ in addition to low CH4 selectivity, with middle isoparaffins as the main products. The catalyst core-shell assembly provided a specific reduced reaction microenvironment with spatial confinement and shape selectivity, in which isoparaffins evolved from the outer surface of the core-shell catalyst pellet scarcely moved into another pellet via the surface zeolite shell because of the huge steric hindrance, thus ensuring increased isoparaffin selectivity.

Recent escalating problems with petroleum supply have encouraged substantial focus on the more efficient syngas to gasoline-range isoparaffin conversion processes. A polygonal barrel-sputtered metallic bi-functional catalyst was synthesized consisting of vastly dispersed Ru nanoparticles (NPs) and H-Beta zeolite as support for one-step synthesis of isoparaffins (gasoline-range) from syngas. This Ru/H-Beta catalyst had high dispersion of metal (31.2 %) with a tapered diameter of 2-4 nm based on high resolution transmission electron microscopy (HRTEM) and chemisorption analysis, and could be directly utilized in F-T synthesis without reduction pre-treatment to achieve CO conversion 1.6 times that of the impregnated catalyst. The highest yield of gasoline-ranged hydrocarbons (C10/Cn ratio = 4.6) depends on the constricted distance between the sputtered Ru particles and the nearby acidic sites. The selectivity for C5-C11 hydrocarbons was very high compared to CH4 and C12+ over the sputtered catalyst, and depended on the highly dispersed Ru nanoparticles and weak interaction between deposited Ru and H-Beta.

A new synthesis pathway was proposed to solve the problems resulting from robust metal-support interaction (MSI) in heterogeneous catalysis based on this catalyst design method. The strong metal-support interactions (SMSI) between the F-T metallic site and support severely restricted reduction of the F-T catalyst, resulting in suppression of H2 and CO chemisorptions after reduction at high temperature. A self-made polygonal physical sputtered ultra-stable Y (USY) zeolite sustained cobalt catalyst was prepared for direct synthesis of gasoline-ranged isoparaffins (C5-C11) from syngas via the modified F-T synthesis reaction. The Co/USY-S catalyst prepared by the physical-sputtering method showed higher metal dispersion and reducibility with more nano-Co0 atoms than that of the conventional impregnated catalyst due to the weak interaction between Co atoms and zeolite support. Therefore, the sputtered Co/USY-S catalyst achieved much higher CO conversion and isoparaffins (C5-C11) selectivity than the catalyst prepared by conventional impregnation. CO conversion was 71 % for the sputtered Co/USY-S catalyst compared to 42 % for the impregnated catalyst. In addition, F-T catalytic activity on Co/zeolite catalysts (H-MOR and H-Beta) was also compared under the same conditions (see Table 1), showing that sputtered catalyst F-T activity was very similar (71-75 %) using three dissimilar molecular sieves as support, demonstrating that conversion of CO was less dependent on the zeolite type. Improved product distribution was attained by adjusting the F-T reaction conditions to raise CO conversion to the same level for Co/USY-I-400 and Co/USY-S-260. Under iso-conversion of around 50 %, the sputtered Co/USY-S-260 exhibited very high C10/Cn value of 1.02, marginally exceeding 0.74 for Co/USY-I-400. The general conclusion was that more reserved acid amount could have been responsible for the enhanced selectivity for isoparaffin in sputtered catalysts.

A high-performance F-T catalyst with high target product selectivity was designed to directly produce target-range (gasoline) liquid fuels in a more energy-efficient and cost-effective way than the multiple-stage procedure. Uniformly sized cobalt nanocrystals were embedded into SiO2 supports with a mesoporous structure (structured like water-melon seeds inside the pulp) and hydrocarbon product selectivity was tuned from 66.2 % diesel-range (C10-C20) to 62.4 % gasoline-
range (C5-C11) by controlling the uniform crystallite sizes of the confined cobalt from 7.2 to 11.4 nm. This phenomenon is quite different from previous observations. Furthermore, the confined cobalt catalyst crystallite size could fundamentally affect the catalytic behaviors in F-T synthesis. Cobalt crystallites were enlarged (d(Co0)T) from 7.2 nm for Cat-4h to 11.4 nm for Cat-12 h, with turnover frequency increasing from $3.9 \times 10^{-2}$ to $6.4 \times 10^{-2}$ s$^{-1}$, as shown in Table 2, but reversibly changing major product selectivity from long-chain C10-C20 with 66.2 % selectivity to short-chain C5-C11 with 62.4 % selectivity, so reversing the conventional ASF rule which indicated that larger metal particles favor long-chain hydrocarbons and vice versa.

Tuning of product distribution was also attempted by manipulating the complex F-T reaction pathway through building bifunctional catalysts with product distribution not following the ASF distribution\textsuperscript{21).} The integrated catalytic route utilizes mesoporous Y-type zeolite (Y$_{\text{meso}}$)-sustained cobalt catalysts (Co/Y$_{\text{meso}}$), prepared via ion exchange, to selectively produce three different liquid fuels (gasoline, jet fuel and diesel) without the hydro-refining post-treatments of F-T waxes, and achieved excellent selectivities for gasoline, jet fuel and diesel. Ce ion-exchanged Co/Y$_{\text{meso}}$-Ce catalyst reached as high as 74 % selectivity for gasoline. Moreover, Co/Y$_{\text{meso}}$-Ce showed excellent stability for CO conversion and gasoline selectivity. The excellent performances of these catalysts were mainly due to the porous and acidic properties of the ion-exchanged Y$_{\text{meso}}$ zeolite, which significantly tuned the product distribution. This work will be discussed further in the section below.

### 4. Jet Fuel (C8-C16) Direct Synthesis via F-T Synthesis

Jet fuel has recently become a significant component (ca. 12 %) of modern liquid transportation fuels mainly due to the rapid global evolution of the airline industry\textsuperscript{21,22).} Conventionally, jet fuel is derived from distillation of crude oil and provides the energy to power gas-turbine engines in aircraft and acts as a primary cooling agent for aircraft and engine subsystems\textsuperscript{22).} The limitations of the ASF product distribution mean that direct production of jet fuel via F-T synthesis is remarkably complex as the ASF curve peak is typically in the range of C6-C8\textsuperscript{9).}

We previously designed a Co/ZrO$_2$-SiO$_2$ catalyst with specific bimodal structure for jet fuel production in F-T synthesis using the incipient wetness impregnation method\textsuperscript{9).} A series of unimodal Co/SiO$_2$ catalysts were also prepared for comparison. Co/ZrO$_2$-SiO$_2$

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### Table 1 F-T Synthesis Performance of Different Prepared Catalysts

| Catalyst     | CO conversion [%] | Selectivity [%] | CH$_4$ | C5+ | C$_{iso}$/C$_n$ | C$_{iso}$/C$_n$ |
|--------------|------------------|----------------|-------|-----|---------------|---------------|
| Co/USY-S-260\textsuperscript{b)} | 71               | 21             | 33    | 0.45|
| Co/USY-I-260 | 42               | 35             | 33    | 0.60|
| Co/USY-I-400 | 52               | 32             | 26    | 0.74|
| Co/MOR-S-260 | 71               | 16             | 51    | 0.59|
| Co/MOR-I-400 | 70               | 18             | 43    | 0.33|
| Co/Beta-S-260 | 75              | 21             | 51    | 1.77|
| Co/Beta-I-400 | 74              | 17             | 60    | 0.90|
| Co/USY-S-260  | 50              | 28             | 42    | 1.02|
| Co/USY-I-400  | 50              | 32             | 26    | 0.74|

F-T synthesis conditions: 260 °C, 1.0 MPa, and $W_{\text{catalyst}}/F = 10$ (g h)/mol. “S” indicates sputtered catalyst while “I” means impregnated catalyst.

a) $C_{iso}/C_n$ is the molar ratio of all isoparaffins to all normal paraffins with $n > 3$.

b) The last number stands for the reduction temperature (°C).

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### Table 2 F-T Synthesis Activity Data of the Water Melon-type Structure Catalysts

| Catalyst | CO conversion [%] | TOF [s$^{-1}$] | Selectivity [%] | CH$_4$ | C2-C4 | C5+ | C5-C11 | C10-C20 | C21+ |
|----------|------------------|----------------|----------------|-------|-------|-----|--------|--------|------|
| Cat-12h  | 80.6             | 0.064          | 8.7            | 11.3  | 80.0  | 62.4| 23.7   | 5.7    |
| Cat-8h   | 78.2             | 0.049          | 10.4           | 14.7  | 74.9  | 42.4| 39.3   | 6.4    |
| Cat-4h   | 77.0             | 0.039          | 8.0            | 7.8   | 84.2  | 15.6| 66.2   | 7.8    |
| Cat-IM   | 84.0             | 0.065          | 18.0           | 14.7  | 67.3  | 43.5| 29.7   | 5.1    |

Reaction conditions: $P = 2$ MPa, $T = 220$ °C, $W/F = 5.1$ g$_{\text{cat}}$ h mol$^{-1}$, CO/H$_2 = 1/2$. 

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catalysts with different pore sizes showed large differences in reactant and product mass transfer, so influencing product selectivity and catalytic activity. Large pores in the Co/ZrO₂-SiO₂ bimodal catalyst enhanced diffusion efficiency, accelerating mass transportation of the reactants and products, whereas small pores increased the surface area of the support for better metal dispersion. Additives of different pure (1-decene, 1-octene, or 1-tetradecene) or mixed 1-olefins (1-octene and 1-decene, or 1-decene and 1-tetradecene) were co-fed with syngas into reaction system to optimize the jet fuel selectivity in the F-T reaction, and suppress the formation of undesirable light hydrocarbons (CH₄, CO₂ and C₂-C₄). 1-Olefins stimulated C-C chain propagation, resulting in shift of the product distribution towards the jet fuel range, thus contradicting the ASF limitations. All types of 1-olefin addition were found to enhance jet fuel selectivity up to 65 % or more. The mixture of 1-decene and 1-tetradecene (volume ratio = 1 : 1) provided the highest jet fuel selectivity of 83.3 % and the lowest light hydrocarbons selectivity among all co-fed mixed 1-olefins.

We also successfully fabricated mesoporous Y-type zeolite supported Co catalysts to selectively synthesize three distinctive and valuable liquid fuels from syngas in an integrated catalytic process ⁷¹. The series of Co/Ymeso-Ce, Co/Ymeso-La and Co/Ymeso-K catalysts were prepared by separate ion exchange of Ce⁴⁺, La³⁺ and K⁺ into the parent mesoporous Y-type zeolite. The Co/Ymeso-Ce, Co/Ymeso-La and Co/Ymeso-K catalysts achieved excellent selectivities of 74, 72 and 58 % for high quality gasoline (with high isoparaffin content), jet fuel and diesel fuel, respectively, via the direct F-T route as shown in Fig. 3. The remarkable performance of these catalysts was mainly attributed to the pore structure and acidity of the Y-type zeolite tuned during ion exchange. Co/Ymicro-Ce, Co/Ymicro-La and Co/Ymicro-K catalysts with microporous support, prepared using the same methods were used for comparison.

The structural characterization results revealed that Co/Ymeso-Ce and Co/Ymeso-La had more moderate Brønsted acidity because of the presence of Ce and La ions whereas Co/Ymeso-K showed no Brønsted acidity. After NH₄⁺ ion exchange, Co/Ymeso-H catalyst exhibited stronger Brønsted acidity. The strong acidity possibly led to over cracking of hydrocarbons, so the selectivity of undesirable C2-C4 products was considerably higher.
straight chain alcohols) and olefin selectivity were highest for Co/Ymeso-H. These observations suggest that acid density had strong influence on product selectivity. Comparison of microporous and mesoporous Y-zeolite supported Co catalysts proved that the mesoporous structure is another key factor in the optimization and control of product distribution.

Furthermore, we managed to develop a new product-distribution model, determined by bifunctional catalytic systems, that also considers the degree of C–C cleavage of heavier hydrocarbons. Common to other bifunctional catalysts, the product distribution of the Co/Ymeso catalysts also deviates from the ASF model. Therefore, our group proposed to introduce the heavy hydrocarbons cracking degree (β) while maintaining the single-α-model of chain growth index, and consider both parameters (α, β) to build a model to best depict the product distribution of F-T-based bifunctional catalytic systems. The establishment of this new model will provide a theoretical basis for the improvement of F-T catalyst design strategies.

5. Syngas Conversion to C2+ Oxygenates via F-T Synthesis

F-T synthesis can also allow one-step synthesis of oxygenated organic compounds, which include alcohols and ketones. The F-T technique utilizes nonprecious metal catalysts for high alcohols (CₙH₂₊ₓOH, n ≥ 6) and high-quality fuel synthesis with low selectivity of light alkanes. High alcohols are used extensively as feedstocks for several commercial products such as plasticizers, detergents, and lubricants.

The impregnation method was used to prepare an iron-based (FeCu/MnO₂) catalyst supported on mesoporous MnO₂ (with small potassium amounts) and added Cu promoter²⁵. The FeCu/MnO₂ catalyst was used to obtain oxygenates and heavier olefins from syngas via the F-T process. CO conversion, oxygenates (mainly straight chain alcohols) and olefin selectivity were highest at 90 %, 74.9 wt% and 71 mol% respectively, using conditions T = 300 °C, P = 1.0 MPa and Fe loading = 20 wt%. The remarkable performance and obvious deviation of the product distribution from the ASF distribution were attributed to the presence of Cu, which enabled ease of formation of a large number of F-T active (Fe₅O₈ and FeC₃) phases at low temperatures. On the other hand, the potassium in the support increased the CO/H₂ ratio by enhancing CO chemisorption while suppressing that of H₂. This resulted in high olefin selectivity which was beneficial as the ethylene precursor reabsorbed onto the active site, initiating a new chain growth reaction by consuming — CH₂— species for C2+ oxygenate synthesis via CO insertion into the alkyl-metal bond or hydroxyl group addition to an alkylidene species.

Recently, great efforts have been made to explore efficient catalysts and technologies to achieve economic viability for high alcohols synthesis on the industrial scale. F-T metal (Fe, Co) modified Cu-based methanol synthesis catalysts can achieve efficient hydrogenation of CO into high alcohols because of their strong promotion of carbon chain growth²⁴. A bimodal support modified Cu-Fe catalyst was prepared by incipient wetness impregnation and used for the synthesis of high alcohols²⁵. Compared to the conventional Cu-Fe catalyst, the bimodal supported (Cu-Fe-K-Meso) catalyst showed higher selectivity (63 %) and activity (CO conversion = 56 %) for high alcohols synthesis under reaction conditions of 320 °C, 5 MPa, 6000 h⁻¹ and H₂/CO = 2. Higher BET surface area improved the dispersion of active Fe and Cu species inside the support pores, and smaller pore sizes of the support resulted in shortened distances between Cu and Fe species due to the confinement effect of bimodal pore structures. These characteristics might have strengthened the synergistic effect between the bimetallic Cu-Fe species, enhancing the insertion of CO* into *CH₃species for improved C2+ OH formation.

6. Conclusion and Outlook

Production of fuel and commodity chemicals from alternative carbon resources has recently become an extremely important research area, due to rising concerns with oil energy depletion and growing environmental demands. This review describes our group’s recent efforts (2011-2019) on the design, fabrication and application of heterogeneous catalysts for the synthesis of liquid fuels and valuable chemicals using the Fischer-Tropsch (F-T) synthesis. However, the product distribution of F-T synthesis is restricted by the ASF distribution. To avoid the costly subsequent refining treatments required to obtain any specific range of hydrocarbons with high selectivities, researchers have continuously modified F-T catalysts to break the limits of the ASF distribution, and remarkable progress has been achieved.

One positive modification strategy has been the coupling of the conventional F-T catalyst with an acidic zeolite to construct a bifunctional catalyst using various methods such as zeolite encapsulation, hydrothermal crystallization, impregnation, metal-sputtering, and others. Bifunctional catalysts can regulate the product distribution through tandem catalytic reactions coupled by some synergistic effect such as lowering byproduct selectivity or absorbing reaction heat in-situ. The assembly methods of bifunctional catalysts, zeolite acid strength and pore structures, have different mechanisms and their effects require further investigations. Moreover, the reaction mechanism becomes more complex if multiple reactions (more than one active site) are involved, so further research is required. Overall, the
concept of bifunctional catalysis is a promising methodology for tuning the F-T product distribution, so breaking the limits of the ASF distribution.

Another approach has been the use of support materials such as reduced graphene oxide or mesoporous carbon, which are weakly interactive toward F-T active sites, to counteract the drawbacks of low activity and mechanical stability in conventional catalysts, so optimizing the F-T synthesis reaction. In addition, adjusting catalyst compositions by adding metal auxiliaries and optimizing reaction conditions remain key factors for improving catalytic performance. Various catalysts improved by these methods were successfully applied in the F-T synthesis of light olefins, gasoline, jet fuel and C2+ oxygenates. Direct synthesis of these target products was effectively realized, breaking the limits of the ASF distributions. We believe that the present methods of catalyst design and mechanisms will stimulate the development of new catalysts and promote research on one-step F-T catalysis with high selectivities.

In conclusion, the efficient conversion of syngas into fuels or commodity chemicals is a highly attractive but challenging target. The synthesis of high-performance catalysts and the precise control of product selectivity have not been fully attained. However, present review of developments in catalyst design and new reaction processes explains more understanding of the nature of active sites, as well as the structure-to-efficiency relationship between catalysts. Future efforts should be directed towards further study of the active catalytic sites and dynamic behavior throughout the catalytic process. Continuous advances in the design of low-cost new active catalysts with improved performance are expected.

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新型フィッシャー・トロプシュ合成触媒の設計による炭化水素合成の制御

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フィッシャー・トロプシュ（F-T）合成は長年にわたって非石油系燃料の中核的な製造技術である。しかし、F-T合成の炭化水素生成物の広い分布は従来古典的なASFを主導する。ASFの制限を打破するために触媒および触媒反応経路の革新は非常に重要である。我々は従来のF-T軽油と異なる製品である軽質オレフィン（C2-C4）、ガソリン（C5-C11）、ジェット燃料（C8-C16）、およびその延長である含酸素化合物をF-T法で合成することを研究してきた。これからの付加価値の高い、かつ需要も多い新製品を選択的に合成するために、いくつかの新しい反応経路を実現できる高性能F-T合成触媒を設計し、ASFの制限を破る炭化水素の生成分布を制御できた。ここではこれらの新型F-T反応群を実現できた高性能触媒の設計思想、および触媒の構造-性能関係を制御する要因を解説する。