Efficient and New Production Methods of Chemicals and Liquid Fuels by Carbon Monoxide Hydrogenation

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ABSTRACT: Carbon monoxide (CO) hydrogenation is an important step for efficient utilization of carbon resources in C1 (one carbon) chemistry. Over recent years, this direction has been a hot research area in academia and industry and has also been one of the most challenging routes for the nonoil carbon resources utilization process. A large number of novel reaction routes and catalysts have been studied and reported. Efficient activation and directional conversion of CO are key aspects in the process of CO utilization. Furthermore, effectively activating C–O and C–C bond formation as well as controlling carbon chain growth is the current technical bottleneck of CO hydrogenation. This mini-review introduces the latest research progress for different catalyst systems and processes in CO hydrogenation and analyzes the factors that control the performance of catalysts in different reaction systems. Here, much focus is put on the synthesis of long-chain hydrocarbons, light olefins, C2+ oxygenates, and aromatics, essentially in comparison with the previous reports. Finally, the present challenges and future research directions have been discussed.

1. INTRODUCTION

C1 chemistry refers to the chemistry of molecules containing a single carbon atom, such as carbon monoxide, carbon dioxide, methane, and methanol, which plays an important role in energy conversion and the value-added chemical preparation platform.1 Conversion of carbon monoxide and hydrogen (syngas: CO + H2) has been extensively studied. Syngas can be prepared easily from abundant and cheap natural carbon resources by reforming natural gas, gasification of biomass, coal, or combustible garbage. By activating C–O bonds and regulating the formation of C–C bonds, syngas can be converted into a variety of petroleum-based chemicals with added value which include light olefin (C2–C4), gasoline (C5–C11), jet fuel (C8–C16), diesel (C10–C20), aromatic hydrocarbons, and oxygen-containing compounds. These compounds critically determine the direction of the chemical and energy industries. In 1936, a synthetic fuel preparation plant was established in Germany to use coal-derived syngas as a raw material. In the decades that followed, factories were built in countries as diverse as South Africa and Malaysia, with some of them producing more than one million tons per year. In an era when energy supply was rife, research on syngas conversion was developed rapidly, as an alternative energy source for oil.2 Due to the continuous exploitation of petroleum resources, reserves of light and low-impurity crude oil rapidly decrease, leaving more aromatic-rich heavy oils with higher impurity concentrations. Syngas, as a substitute of petroleum energy, is of great significance in producing chemicals and liquid fuels, and its introduction allays anxiety and uncertainty over the energy factor of the future. Recently, several teams have made breakthroughs in the field of syngas conversion.

It is well-known that the main pathways of syngas conversion are Fischer–Tropsch (FT) synthesis reaction (direct), methanol synthesis, and methanol to hydrocarbon (MTH) synthesis reaction (indirect), being operated in industry. Catalysts play a crucial role in FT synthesis. FT synthesis is a classic syngas to hydrocarbon pathway first proposed and named after Hans Fischer and Franz Tropsch in 1925. FT synthesis converts syngas into a series of hydrocarbons through a heterogeneous catalytic process. A widely accepted reaction process is that CO and H2 are adsorbed and activated on the surface of the catalyst to form CHx (x < 3) particles. Through the coupling of CHx species, the coupling of C–C bonds forms the intermediate product CnHm (n ≥ 2), to realize the growth of the carbon chain. Methane is also formed as a byproduct when CHx is hydrogenated. The intermediate CnHm is further hydrogenated to an alkane or dehydrogenated to an alkene. Due to the sufficient supply of H2, the n-alkane of the long chain is the main product of this process, and the carbon number distribution of the product follows the distribution law of Anderson–Schulz–Flory (ASF). According to the distribution rule of ASF, the highest selectivity of products is limited to C2−
Ru-based catalysts. Fe-based catalysts are a relatively mature interest to many researchers. Designing a reasonable catalyst is a research direction of great importance to break through the limitation of selectivity of ASF products by saturated alkane. Ru-based catalysts have better catalytic activity than Fe-based and Co-based catalysts, in addition to better anticarbon deposition ability. However, due to its high price and high cost (Ru based), it is not suitable for industrial application. In recent years, scientists have conducted a lot of research on the reaction mechanism and structure of FT catalysts and made a series of substantial progress. Nevertheless, the deactivation caused by carbon deposition of a traditional catalyst and the deactivation caused by carbon deposition of Ymeso zeolites can realize the highly selective synthesis of gasoline, diesel, and jet fuel using nanoscale cobalt particles confined inside the mesoporous Y-type molecular sieve cage as the catalyst for FT synthesis. It is well-known that the addition of suitable alkali metal can improve the activity of catalysts and the realization of carbon chain growth on the FT catalyst, and then product distribution is modified by regulating the acidic and or porous properties of zeolite, where the products are directly synthesized. The second type is the combination of the methanol synthesis catalyst and a zeolite. The intermediate products (such as methanol and dimethyl ether) are first synthesized on the methanol synthesis catalyst and then converted to hydrocarbons. By optimizing the design of either multifunctional catalysts, the product distribution can be precisely controlled.

2. SYNGAS CONVERSION TO LONG-CHAIN HYDROCARBONS (C_{5+})

As more experiments were carried out to break the ASF limitation of FT hydrocarbon distribution, researchers found that secondary cracking occurred in the reaction process. Many catalysts with multiple functions can also accurately optimize product distribution. Researchers have achieved the integrated control of the liquid fuel in the product, obtainable at high yields. Many groups have studied syngas conversion catalysts over recent years, prepared by physical mixing, incipient wetness impregnation, core–shell structure fabrication, or the physical sputtering method. Our research group has designed different types of catalysts to combine a metal, carrier (such as Co/Al_{2}O_{3}, Co/SiO_{2}, fused Fe, etc.), and molecular sieve (H-ZSM5, H-Beta, etc.) to prepare multifunctional catalysts. By adding promoters, regulating the activity of metal, optimizing the acidic amount and strength, or adjusting thickness and pore structure, high liquid hydrocarbon yield could be attained. Based on our previous research, we successfully realized the highly selective synthesis of gasoline, diesel, and jet fuel using nanoscale cobalt particles confined inside the mesoporous Y-type molecular sieve cage as the catalyst for FT synthesis. It is well-known that the addition of suitable alkali metal can improve the activity of catalysts and the

Figure 1. Catalytic performance. (a) Fischer–Tropsch performance over the catalysts with conventional supports or Ymeso zeolites. (b–d) Detailed product distribution of Ymeso catalysts: Co/Ymeso−Ce (b), Co/Ymeso−La (c), and Co/Ymeso−K (d). Reaction conditions: temperature, T = 523 K; pressure, P = 2.0 MPa; H_{2}/CO = 1.0; flow rate, W_{cat}/F = 10 g h^{-1} mol^{-1}; catalyst weight, 0.5 g; time on stream, 10 h. The calculation of hydrocarbon selectivity was based on the weight fraction of a product with respect to the total hydrocarbons. Reproduced with permission from ref 5. Copyright 2018. Nature Catalysis.

C_{4} 58%, C_{5}−C_{14} 48%, C_{15}−C_{20} 41%, and C_{10}−C_{20} 40%. How to break through the limitation of selectivity of ASF products by designing a reasonable catalyst is a research direction of great interest to many researchers.

The conventional FT reaction is dominated by Co-, Fe-, and Ru-based catalysts. Fe-based catalysts are a relatively mature FT catalyst. It has good reaction performance, low price, and low selectivity of methane, while secondary hydrogenation is not easy to occur. This weak carbon chain growth ability and suitable hydrogenation ability of Fe-based catalysts improve the olefin content in the reaction products as previously reported. However, there are still some challenges, such as high CO_{2} byproduct selectivity. Therefore, appropriate additives or optimization of catalyst structure are needed to improve the reaction performance. Compared with Fe-based catalysts, Co-based catalysts have a characteristic high activity, higher C–C chain growth ability, and low water gas shift reaction (WGSR: CO + H_{2}O = CO_{2} + H_{2}) activity. The product is mainly saturated alkane. Ru-based catalysts have better catalytic activity than Fe-based and Co-based catalysts, in addition to better anticarbon deposition ability. However, due to its high price and high cost (Ru based), it is not suitable for industrial application. In recent years, scientists have conducted a lot of research on the reaction mechanism and structure of FT catalysts and made a series of substantial progress. Nevertheless, the deactivation caused by carbon deposition of a traditional catalyst and the difficulty in product distribution regulation still pose great challenges to FT synthesis.
selectivity of C\textsubscript{5+} in the products.\textsuperscript{11,12} We used an ion exchange method to modify the mesoporous Y-type zeolite with Ce\textsuperscript{4+}, La\textsuperscript{3+}, and K\textsuperscript{+}. The acidity and pore sizes of the zeolite were adjusted to obtain Co/Y\textsubscript{meso}−Ce, Co/Y\textsubscript{meso}−La, and Co/Y\textsubscript{meso}−K catalysts. As a comparison, Co/Y\textsubscript{micro}−Ce, Co/Y\textsubscript{micro}−La, and Co/Y\textsubscript{micro}−K catalysts with microporous support were also prepared using the same methods. The reduction degree, metal particle distribution, and particle size of the catalysts were calculated. After performance test, the catalytic reaction results of Co/Y\textsubscript{meso}−Ce, Co/Y\textsubscript{meso}−La, and Co/Y\textsubscript{meso}−K catalysts showed excellent selectivity for gasoline, jet fuel, and diesel, up to 74%, 72%, and 58%, respectively (Figure 1).

Different from the previous regulation of most products, the pore structure and acidity of Y-type zeolite were regulated by ion exchange and implantation of mesopores. Consequently, the high selectivity of various liquid fuels on demand (gasoline, aviation fuel, or diesel) was achieved.

In addition, the characterization results showed that because of the existence of Ce and La particles Co/Y\textsubscript{meso}−Ce and Co/Y\textsubscript{meso}−La catalysts were detected with more moderate Bronsted acidity. No Bronsted acidity was detected in Co/Y\textsubscript{meso}−K. The Co/Y\textsubscript{meso}−H catalyst showed lower reduction degree and stronger Bronsted acidity after NH\textsuperscript{+} ion exchange. Such strong acidity may lead to excessive cracking of hydrocarbons and generate more undesirable light hydrocarbons. It can also be clearly observed in Figure 1a that its selectivity of C\textsubscript{2}−C\textsubscript{4} products was significantly higher than that of other catalysts. This study reveals that the pore structure and acidity of the Y-type zeolite play a key role in the optimization and regulation of product distribution. In addition, since the traditional ASF product distribution law cannot accurately describe the product distribution in many multifunctional catalyst systems, here we establish a new extended model of the ASF distribution model to describe the product distribution in the FT-based multifunctional catalyst. While using the α model of the chain growth index, we propose the concept of cleavage contribution degree β. The product distribution of FT-based multifunctional catalysts is predicted by using the dual key parameter (α, β) model. The establishment of this model is of great help to the design and development of new FT catalysts in the future.

3. SYNGAS CONVERSION TO LIGHT OLEFINS (C\textsubscript{2}−C\textsubscript{4})

Olefins, especially light olefins (ethylene, propylene, butene), are the most basic raw materials in the chemical industry and are among the largest amount of chemicals in the world. The main source at present is petroleum, which is obtained by cracking (FCC). The synthesis of light olefins from syngas provides a new catalytic route which is cleaner and more efficient.

The conventional route of FT synthesis is to modify Co- or Fe-based catalysts with some auxiliary components such as alkali metals and transitional metals (Mn, Ru, etc.), to improve olefin selectivity. According to the distribution law of ASF, the proportion of C\textsubscript{2}−C\textsubscript{4} hydrocarbons in the products cannot exceed 58%, and the selectivity of methane is higher than 29%. This is far from the expected efficient use of syngas, so researchers are constantly trying to break through the product limit in ASF theory by designing catalysts. De Jong’s team applied Fe nanoparticles, evenly loaded onto an α-Al\textsubscript{2}O\textsubscript{3} or carbon fiber, and modified them with promoter to obtain light olefin selectivity of up to 60%, which was beyond the product limit of ASF law, but the selectivity of methane in the products was still higher than 22%.\textsuperscript{6} Sun reported that Co\textsubscript{2}C prism nanoparticles, developed coincidentally or endogenously from the as-prepared nanoscale CoMn during reaction, were found responsible for syngas to light olefin synthesis. The catalyst changed into two phases (Co\textsubscript{2}C and MnO). Unlike conventional spherical Co\textsubscript{2}C, which was not conducive to FT synthesis, the Co\textsubscript{2}C here was prismatic, exposing (101), and (020) crystal planes. These in situ crystal planes resulted in high light olefin selectivity of 60.8%, and low methane selectivity was maintained at 5.0%. The reaction conditions were mild (1 bar, 250 °C), and the syngas with lower H\textsubscript{2}/CO ratio (H\textsubscript{2}/CO = 0.5−2.0) was used as the raw material. After activation of the catalyst for more than 15 h under the reaction conditions, the light olefin selectivity increased from less than 20% to more than 50%, and the selectivity of C\textsubscript{5+} products decreased from about 80% to less than 40%. Stable operation for 30 h was maintained, while methane selectivity was always around 5%. On the product distribution, the CoMn catalyst was quite different from the traditional FT catalyst.

Figure 2. Catalytic process of OX-ZEO. (A) CO conversion and product distribution at different H\textsubscript{2}/CO ratios in syngas over a catalyst with a mass ratio of ZnCrO\textsubscript{x}/MSAPO\textsubscript{y} = 1.4 at a space velocity of 4800 mL/h-gcat. (B) Hydrocarbon distribution in OX-ZEO in comparison to that reported for FTTO and that in FTS predicted by the ASF model at a chain growth probability of 0.46, with the yellow bar representing selectivity of C2−C4 hydrocarbons. Reproduced with permission from ref 6. Copyright 2016. Science.
Bao’s team reported a new multifunctional catalyst named OX−ZEO (oxide−zeolite), which achieved one-step syngas conversion to light olefin with high selectivity and conversion. The catalyst consists of metal oxide ZnCrOx and SAPO zeolite and has a life of over 100 h under 400 °C, 2.5 MPa, and H2/CO = 1.5, which makes it suitable for industrial application. Carbon monoxide and hydrogen are activated on the surface of the metal oxides to form the CHx species and then convert them to ketene (CH2CO). The ketene diffuses into the SAPO zeolite, and at the acidic active site it is converted to light olefins. The selectivity of C2−C4 olefins is 80%; the C2−C4 alkane is 14%; and CO conversion is 17%. Meanwhile, the selectivity of methane is controlled at 2%. It is found by characterization that during FT synthesis there is polymerization among CHx generated on the catalyst surface, and the distribution of C chain length can be described by the ASF model. When the composite metal oxide is partially reduced and used to activate CO, the polymerization of the CHx intermediate on the catalyst surface can be effectively inhibited, and CO can be inserted to form a ketene. This study separates the two processes of CO activation and C−C bond formation to achieve a breakthrough in the selectivity limitation of FT synthesis. The team then reports another multifunctional catalyst, ZnCrOx−MOR, which can achieve a highly selective synthesis gas to ethylene conversion. Ethylene selectivity in hydrocarbon products is up to 80%. It is found that the Brunsted acid located in the 8-membered ring of MOR zeolite is the active center of ethylene production. The intermediate ketene is more likely to be adsorbed in the 8-membered ring, while methanol is more likely to be adsorbed in the 12-membered ring (Figure 2).

Ma reported that the Fe−Zn−Na catalyst obtained by modifying Fe3C2 with Zn and Na achieved CO conversion of 63.0% at 340 °C and 2 MPa. The selectivity of C2−C4 hydrocarbons and C6+, hydrocarbons was 22.6% and 46.3%, respectively. The ratio of olefin to paraffin was as high as 7.4, and the CO2 selectivity was maintained at 22.5%. When the CO conversion reached to 82.7%, C2−C4 and C6+, hydrocarbon selectivity was maintained at 22.6% and 46.3%, respectively, and the selectivity of CO2 was only 11.7%. It was found that Na had a crucial effect on the performance of the catalyst in the FT reaction. Na could transfer electrons to Fe on the surface of the catalyst and change the electronic structure of Fe5C2. The reaction of CO and hydrogen on the surface of Zn−CrO2 is key to the production of light olefin. In this process, formate and H species formed methoxide slowly, which determined the rate of the whole reaction. The reaction path on the oxide surface was CO adsorption → formate → methoxide → methanol/dimethyl ether → light olefin (Figure 3).

4. SYNGAS CONVERSION TO C2+. OXYGENATES

C2+ oxygenates are a kind of chemical raw material with high value, such as alcohols, aldehydes, ethers, and esters, containing two or more carbon atoms in a molecule. The C2+ alcohol, also known as high alcohol, is expected to be used directly as a fuel or as a clean gasoline additive. Industrial high alcohol is also an important basic raw material, or chemical intermediate, which can be synthesized to surfactant, detergent, plasticizer, and a variety of other fine chemicals. In recent years, important progress has been made in the preparation of C2+ oxygenates through catalyst design and selectivity regulation. In the synthesis of high alcohols, modified methanol catalyst, modified FT catalyst, Rh-based catalyst, and Mo-based catalyst have been widely studied. It is generally accepted by researchers that during the synthesis of high alcohols both the chain growth center and the oxygen-containing species insertion center are needed on the catalyst surface, and the contact boundary of the active center is more conducive to form the oxygen-containing products. However, the reaction mechanism of high alcohol synthesis is complex, and there are many competitive reactions and side reactions, resulting in many byproducts. In addition, the hydrogenation of CH2 intermediate species has a lower thermodynamic barrier than CO insertion, resulting in a generally low selectivity of C2+ oxygenates.

Sun reported a CoMn1CuZnAlZr catalyst for syngas conversion to C2+ oxygenates. When the CO conversion was 29%, the selectivity of oxygenates reached 58.1 wt %, where the C2+ oxygenate content exceeded 92.0 wt % and the total selectivity of oxygenates and olefin in the product reached 80.6 wt %. The researchers found that in the CoMn1CuZnAlZr catalyst product distribution was affected by spatial structure.
and that, when reasonably regulated, the spatial structure of the metallic site could significantly control product distribution. Therefore, the undesirable C1 products (MeOH, CH4, CO2) could be inhibited. It is believed that there exist dual active centers on Co/Co2C in the synthesis of high alcohols. The CuZnAlZr catalyst can change the microenvironment around the active center and provide a large number of CHxO* species, which is conducive for CO diffusion to the surface of CoMn and the insertion reaction and then promote the generation of oxygenates (Figure 4).

Our group reported a capsule zeolite catalyst with core−shell structure (Figure 5A).18 Silicalite-1 or H-ZSM-5 zeolite as shell is allowed to grow naturally on the Cu/Zn/Al2O3 core through hydrothermal synthesis to obtain CZA-Z and CZA-S core−shell structure catalysts. The aluminum migration method was used such that the core catalyst played a role as the aluminum resource in the hydrothermal process. This catalyst design could effectively regulate the reaction sequence, break the thermodynamics equilibrium limitation of the methanol synthesis process (whose comprehensive reaction mechanism was investigated by Xu et al., in 200919), and promote the conversion of syngas. Meanwhile, the zeolite shell provided a good dehydration environment for methanol, which greatly improved the selectivity of dimethyl ether. Compared with the traditional physical mixed catalyst, the selectivity of dimethyl ether increased from 40.51% to 96.59%, and the methanol selectivity decreased from 57.29% to 3.41%. Using CZA-S catalyst, the selectivity of dimethyl ether remained at 78.57% when the CO conversion was maintained at 30.40%. According to the continuous reaction concept, synthesis gas → dimethyl ether → methyl acetate → ethanol, we first invented a multifunctional catalyst to realize ethanol synthesis from syngas and dimethyl ether by coupling Cu/ZnO and H-MOR zeolite.20,21 However, Cu-based catalysts suffer from some limitations because of the tendency of copper to sinter at high temperatures (Cu more effective ≤ 250 °C). It was also found that metallic agents (Ru, Pd, Pt) could promote carbonylation. When the reaction conditions were 493 K and 1.5 MPa, the carbonylation of dimethyl ether on a separate H-MOR zeolite catalyst obtained a selectivity of up to 92.2% methyl acetate with a yield of 1076.1 mmol kg−1 h−1. The conversion of dimethyl ether was 83.1%, and the selectivity of CO2 was lower than 5.4%. When Cu/ZnO was added as the second stage catalyst, the ethanol selectivity could be maintained at about 41.0%.

In the process of carbonylation of dimethyl ether, H-MOR zeolite would be affected by the presence of water which inhibits carbonylation reaction. Wang further designed the Cu−Zn−Al/H-ZSM-5|H-MOR catalyst.22 The addition of H-ZSM-S separated Cu−Zn−Al from H-MOR zeolite and promoted the further occurrence of water–gas shift (WGS) reaction in water. The carbonylation rate was guaranteed after water consumption, and the activity of the catalyst was significantly improved. The selectivity of methyl acetate obtained under 473 K and 3 MPa was up to 95%. Further study found that the combination of ZnAl2O4 with spinel structure and H-MOR

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**Figure 4.** Proposed reaction pathway for oxygenate formation over the multifunctional catalyst. Reproduced with permission from ref 17. Copyright 2019. Angewandte Chemie International Edition.

**Figure 5.** (A) Schematic diagram of dimethyl ether direct synthesis from syngas on a single zeolite capsule catalyst. Reported by ref 18. Copyright 2010. Journal of American Chemical Society. (B) Direct conversion of syngas into methyl acetate, ethanol, and ethylene by relay catalysis using combinations of catalysts with different functions. Reported by ref 22. Copyright 2018. Angewandte Chemie International Edition.
zeolite (ZnAl₂O₄·H-MOR) could realize the highly selective conversion of syngas to methyl acetate and acetic acid at high temperature (340−370 °C). When CO conversion was 11%, the total selectivity of methyl acetate and acetic acid was up to 87%. Using a three-layer structure catalyst ZnAl₂O₄·H-MOR/ZnAl₂O₄ could directly convert syngas into ethanol, and the selectivity was 52%. The multiple layer catalyst ZnAl₂O₄·H-MOR/ZnAl₂O₄·H-MOR was capable of producing ethylene from syngas because ethylene can continue to dehydrate on the added H-MOR zeolite. The selectivity of ethylene was about 50%. Mixing the terminal ZnAl₂O₄ with H-MOR zeolite could further improve the ethanol dehydration efficiency, and the ethylene selectivity could improve to 65% (Figure 5b).

5. SYNGAS CONVERSION TO AROMATICS

Aromatics are important raw materials for the chemical industry and can be used to prepare many fine chemicals. The aromatic products are a hydrocarbon mixture with benzene ring structure. In industry, they are mainly used in the production of synthetic fibers, synthetic rubber, and synthetic resin, to mention a few. Aromatics can also be used as gasoline additives with high octane number. Traditionally, aromatic hydrocarbons are produced from petroleum or prepared by catalytic reforming. It is however very imperative and of high research value to develop a new synthetic route for aromatics.

Ma and Fan reported the route of synthesizing aromatics from syngas with olefin as an intermediate. Based on a study involving the Na−Zn−Fe₅C₂ catalyst, researchers mixed this catalyst with some mesoporous zeolite of H-ZSM-5. Fe₅C₂ (in Na−Zn−Fe₅C₂) was the active phase for alkene synthesis. In essence, Na acted as an electronic promoter by enhancing the fundamental surface reactions to produce more alkenes, at the same time suppressing hydrogenation of olefins by weakening their adsorption on the catalyst surface. HZSM-5 attained a mild Bronsted acidity micromesoporous (hierarchical) state after modification which greatly improved the mass transfer of reactants and products on the catalyst. At 340 °C, 2 MPa, about 50.6% aromatics were obtained in the hydrocarbon products. The selectivity of CO₂ was inhibited to 27.5%, while the selectivity of methane was 9.6%. The total aromatics yield was over 32.3%. Ding reported a bifunctional catalyst with hollow structure of H-ZSM-5 and Fe₅O₄@MnO₂ to realize the direct synthesis of aromatics from syngas. When the aromatics' selectivity was 56.6%, CO conversion could be as high as 90.3%. No significant deactivation of catalyst was observed during the 180 h test. For the Fe₅O₄@MnO₂ catalyst, the confinement effect of the core−shell structure and the influence of Mn additives promoted the conversion of syngas into olefin intermediate species, which was effectively converted into aromatic target products on the acidic active site within hollow H-ZSM-5. The suitable H-ZSM-5 channel and hollow structure were conducive to the diffusion of reactant and product molecules and promoted the generation of aromatics. The concentration of carbon deposition in the pore channel of the zeolite was inhibited, and the stability of the catalyst was significantly improved.

The new catalysts from the recent studies have yielded surprising results on the efficient synthesis of aromatics from syngas. However, there are still few studies on the preparation of single aromatic hydrocarbons with added value, from syngas. Among aromatic compounds, para-xylene (PX) is an important chemical with added value. Wei used the Zn/P/Si/ZSM-5 catalyst and methanol as the starting material to prepare PX with high selectivity. Through modifying the surface, the internal acidity in the catalyst was strong, and the surface acidity was weak. This acidic gradient assumed therein could inhibit hydrogen transfer on the catalyst surface, thereby extensively restricting hydrogenation and isomerization side reactions. The yield of aromatics from MeOH was over 60%, and the selectivity of PX was improved from the usual 23−24% to 89.6%. Our group designed a new type of Cr/Zn−Zn/ZS@S1 hybrid catalyst to first realize directional conversion of syngas to PX. This catalyst is comprised of two parts, i.e., Cr/Zn oxide catalyst and Zn/ZS@S1 with core−shell structure, which could escalate PX selectivity to 77.3% in the xylene isomers and 27.6% selectivity in total hydrocarbon products at CO conversion of 55.0% (Figure 6). At the same time, the selectivities of CH₄ and

C₅−C₆ hydrocarbons were lowered to 4.4% and 33.6%, respectively, which makes it obvious that isomerization side reactions were greatly interrupted. This catalyst could combine the tandem reaction of syngas to methanol and methanol to PX. There existed an interaction between the two active components in the catalyst. The syngas was first converted to the methanol intermediate on the Cr-based catalyst, and the methanol intermediate diffused to the active site within the zeolite to generate PX. This special Zn/ZS@S1 core−shell structure effectively protected the acidic sites of zeolite, avoiding their overexposure at the outer surface of zeolite, inhibiting the formation of undesirable xylene isomers and promoting the directed synthesis of PX. However, the catalyst still suffers from the formation of numerous byproducts.
(alkane/alkenes and other aromatic compounds). Thus, other investigations around the thickness of the silicalite-1 zeolite shell coating on the Zn/Z5 core zeolite could further weaken side reactions.

6. CONCLUSIONS AND OUTLOOK

In the past decades, due to concerns of oil energy exhaustion and increasing environmental requirements, the efficient and green conversion of syngas has attracted extensive attention in academia and industry. Here, the research progress of high efficiency catalysts in syngas conversion is reviewed. These new catalysts and novel reaction routes are of great importance. The mechanisms of reaction and catalyst structure need to be further studied as there are still many new challenges.

First, some new multifunctional catalysts for long-chain hydrocarbon selective synthesis from syngas, breaking the distribution limit of the ASF law, were summarized. The multifunctional catalysts were prepared by combining different metal auxiliaries and alumina or porous materials such as zeolite. The intermediate products such as dimethyl ether/light olefin and others could be regulated by adjusting the acidic active sites of the zeolite in the catalyst, and the secondary reaction of intermediate products was optimized to promote the concentration of products. However, the product distribution still needs to be further adjusted to obtain a more reasonable ratio of alkanes, isomeric alkanes, cycloalkanes, and other products.

The synthetic route of syngas to olefin and C2+ oxygenates was also summarized. The catalysts reported in this part mainly combined the FT catalyst or methanol synthesis catalyst with zeolite. After addition of zeolite, the selectivity of the products could be significantly improved. However, compared with the traditional FT synthesis, the single-pass conversion rate was generally lower. The strong interactions between metals have a significant effect on catalyst activity, as well as interactions between metals and zeolite, which means the catalyst design should be more prudent. Catalyst composition, spatial distance, acid strength, pore structure, and reaction conditions are key factors to be investigated. However, it is still challenging to improve the single-pass conversion and the stability of catalysts while maintaining a high selectivity. In addition, the reaction mechanism in relation to catalytic performance becomes more complicated when involving the combination of multiple reactions; therefore, further research and exploration are also needed.

Finally, the synthesis of aromatics from syngas was introduced. Aromatics are mainly synthesized by a petrolem-based route at present. Here, we reported the recent synthesis of aromatics (PX) via the FT route or methanol route. Because aromatic hydrocarbons are one of the most important chemicals, these novel synthetic pathways are quite impressive. However, researchers are still faced with severe challenges. In the process of reaction, synthetic gas has to go through methanol/light olefin synthesis, hydrogen transfer, oligomerization, cyclization, dehydrogenation, and other reactions, and the whole process is quite complicated. The selectivity and stability of the product are sensitive due to the Brönsted acid centers and pore structure in the zeolite channel. Achieving high selectivity of the target product is still changing. There are few studies on the synthesis of aromatics from syngas at present, and therefore more research is needed to reveal the mechanism of the whole process.

In conclusion, efficient conversion of syngas is an important energy and chemical conversion platform, which plays a vital role in energy security and chemical industry development. A large number of articles in the field of syngas conversion have been published, which indicate that researchers attach great importance to this field. In the future, further attention should be paid to the relationship between the reaction mechanism, catalyst structure, and performance, especially the pore structure of zeolite, acid regulation, and metal interaction of multifunctional catalyst. Further design of multifunctional catalytic systems and more precise control of product selectivity are expected.

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Noritatsu Tsubaki received his PhD from the University of Tokyo in 1995 and then worked in University of Tokyo as a lecturer and associate professor from 1995 to 2000. In 2001, he moved to the University of Toyama as a full professor in the school of engineering. His research areas include efficient conversion of low carbon resources and preparation of clean energy. He received the Noguchi Prize from Japan Petroleum Institute (JPI) in 1998; JSPS Prize from Japan Society for Promotion of Science (JSPS) in 2006; Highly-Cited Researchers 2016 in the energy field; and Prize of Japan Institute of Energy (JIE) in 2018. He has published more than 500 papers, 75 patents, and 10 book chapters. He was selected as a Member of the Science Council of Japan in 2017.

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