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Perspective

Catalysis for Selected C1 Chemistry

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SUMMARY

Catalytic conversion of one-carbon (C1) molecules, such as CO, CO_2, CH_4, and CH_3OH, into fuels and value-added chemicals is a vitally important process in the chemical industry because of its close correlation to energy and environmental implications. However, the selectivity control, energy saving, and emission reduction remain great challenges for C1 chemistry due to the complex and changeable conversion processes. Herein, we briefly summarize recent advances and milestones in conversion of C1 molecules in the last decade, particularly focusing on the new reaction processes, including thermal-driven reactions, such as direct methane to ethylene, CO_2 hydrogenation, and oxide-zeolite process for syngas conversion, and mild-condition conversion processes, such as room-temperature methane conversion, electrochemical water-gas shift, electrocatalytic CO reduction to ethylene, and light-driven methanol to ethylene glycol. The challenges and prospects are also fully discussed toward the C1 chemistry for the basic and applied research in the future.

INTRODUCTION

One-carbon (C1) chemistry refers to the chemistry of synthesis of a series of important chemicals and fuels from compounds containing one-carbon atom, such as CO, CO_2, CH_4, and CH_3OH. The primary sources of these C1 molecules are coal, natural gas, biomass, or organic wastes. With the dwindling sources of petroleum and the increasingly serious problems of environmental pollution, C1 chemistry has become even more important due to the increasing need for the manufacture of fuels and petrochemical commodities. The current main conversion pathways of C1 molecules are shown in Figure 1. Several representative processes, such as the Fischer-Tropsch synthesis (FTS), water-gas shift (WGS), and methanol steam reforming (MSR), have been well known for several decades. The conversion of C1 molecules typically relies on the process of catalysis, especially heterogeneous catalysis. Great advances in basic and applied research have been made for the development of C1 conversion processes on the basis of the important catalytic systems. However, due to these C1 molecules existing with either the relatively inert nature (e.g., CH_4 and CO_2) or high reactivity (e.g., CO and CH_3OH), there is no unified principle for the C1 conversion, leading to formidable challenges in the balance of selectivity and conversion for C1 chemistry. In addition, the most current C1 conversion processes in industry suffer high energy consumption and have the most complex processes of multi-step reactions and product separations. Therefore, it is highly desirable to develop novel and efficient C1 conversion pathways for oriented production of fuels and chemicals, which requires major innovations in the design of catalysts and development of reaction processes.

Although there are great challenges and difficulties in the conversion of C1 molecules, there has been enormous progress in the development of efficient C1

The Bigger Picture

Challenges and opportunities:

- Controlling the selectivity of products and reducing energy cost and carbon emission are great challenges for C1 chemistry
- Synthesizing highly effective catalysts and exploring novel catalytic processes open paths for the conversion of C1 molecules under mild reaction conditions
- Developing *in situ* and *operando* characterization techniques for the effective identification of the structural evolution of catalysts as well as the deep understanding of the catalytic active centers provides a framework for the synthesis of catalysts

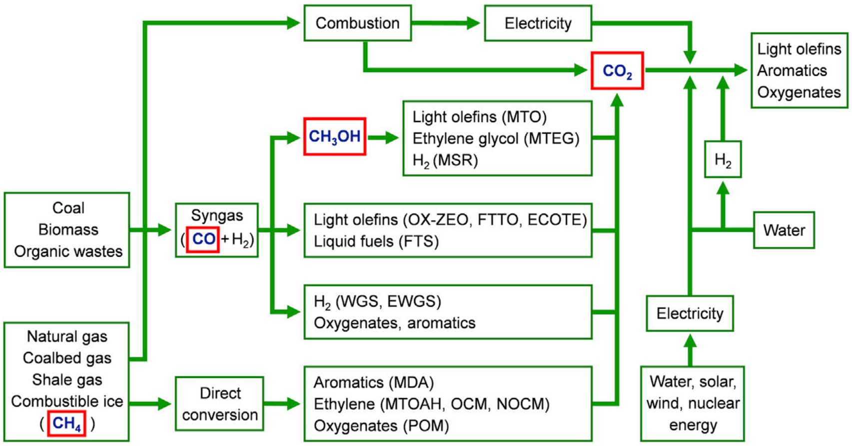

Figure 1. The Origins and Conversion Pathways of the Different C1 Molecules

conversion process in the past few decades, and the progress is particularly pronounced in the last decade due to the dual pressures from speedy consumption of petroleum resources and serious environmental pollution. In this perspective, we briefly summarize advances in conversion of C1 molecules, including CO, CO_2, CH_4, and CH_3OH, in the last decade. Particular emphasis is placed on new catalytic processes, such as direct methane to ethylene, aromatics, and hydrogen (MTOAH), room-temperature methane conversion, oxide-zeolite (OX-ZEO) process for syngas to light olefins, CO_2 hydrogenation to alcohols and hydrocarbons, electrocatalytic CO reduction to ethylene (ECOTE), room-temperature electrochemical water-gas shift (RT-EWGS), and light-driven methanol to ethylene glycol (MTEG). We also discuss the opportunities and challenges in C1 chemistry for future research.

CH_4 CONVERSION

Methane, the main component of natural gas, coalbed gas, shale gas, and combustible ice, is one of the most abundant hydrocarbon resources on Earth. The conversion of CH_4 into value-added chemicals, such as olefins, aromatics, and oxygenates, has received considerable attention because of the growing demand for these chemicals and the recent discovery of large reserves of CH_4 resources.[1] The primary strategies for CH_4 conversion have been classified into two types, namely the indirect routes via syngas and the direct conversion routes. The industrial process for CH_4 conversion is the indirect route, involving the steam reforming methane (SRM) to syngas over a Ni-based catalysts,[2] and the subsequent conversion into high-demand chemicals using the well-established FTS technology (Figure 1).[3] However, major disadvantage of the indirect route is high energy consumption because the SRM process is strongly endothermic ($\Delta H^\circ_{298\ K}$ = 206 kJ mol^{-1}) and usually requires high reaction temperature of >923 K.[4] The direct conversion of CH_4 to chemicals without involving the syngas production step is attractive owing to its simple process. However, because a CH_4 molecule exhibits high C–H bond dissociation energy (BDE) of 439.3 kJ·mol^{-1}, low polarizability, and negligible electron affinity,[5] efficient activation could easily lead to deep dehydrogenation or overoxidation. In this section, we briefly summarize recent breakthroughs in direct CH_4 conversion via oxidative and nonoxidative routes.

Nonoxidative CH_4 Conversion

Nonoxidative coupling of methane (NOCM) is a desirable process for the synthesis of C_{2+} hydrocarbons, despite being thermodynamically unfavorable. Amariglio et al.

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first found that silica supported Pt catalyst can be active for CH_4 conversion with a 95% C_{2+} selectivity at 523 K.[6] The formation path of these hydrocarbons involves activation of CH_4 on catalyst surface to form H_2- and H-deficient CH_x species through C−H bond dissociation and then the oligomerization of the CH_x to C_{2+} products. However, due to the limit of reaction equilibrium at the reaction temperature employed, CH_4 conversion is extremely low. The high-temperature methane dehydroaromatization (MDA) is an alternative process for converting CH_4 directly. Since it was first proposed by Wang et al. in 1993,[7] zeolites (e.g., ZSM-5 and MCM-49) supporting Mo catalysts have been intensively investigated due to their high activity.[8] However, the mechanism for the MDA over the Mo catalysts remains controversial today despite great progress. Many researchers believe that Mo sites account for the activation of C−H bonds in CH_4 via the formation of Mo carbide phase and convert the resulting CH_x species into C_2H_x intermediates, followed by oligomerization of C_2H_x to aromatics on catalyst Brønsted acid sites.[9] The main drawback for the Mo-containing zeolite catalysts is poor lifespan because of the coke deposition and bad structural stability of zeolites. Recently, Podkolzin and coworkers found that initial Mo oxide monomers anchored on Al sites of the zeolite framework give more active Mo carbide nanoparticles than those produced by initial Mo oxide species anchored on Si sites of the zeolite external surface, and the activity of the catalyst after deactivation can be completely recovered and even increased via regeneration with oxygen.[10]

The key problem for the MDA to be solved is to inhibit deep dehydrogenation while retaining high the first C–H bond-cleaving activity. In 2014, Bao group discovered that single iron sites embedded in a silica matrix (Fe_1©SiO_2) can catalyze CH_4 conversion to olefins, aromatics, and hydrogen (MTOAH).[11] The CH_4 conversion reached 48.1%, and C_2H_4 selectivity exceeded 48.4% at 1,363 K, accompanied by benzene (21.5%) and naphthalene (25.8%) (Figure 2A). Mechanism studies have shown that the unprecedented efficiency attributed the single Fe site account for the cleaving of the first C−H bond in CH_4 and are relatively inactive for C−C coupling, eliminating coke formation. The C_{2+} products were mainly produced from dissociated methyl radicals by gas-phase coupling reactions (Figure 2B). The findings offer a new horizon in the rational design of catalysts and the fundamental understanding of the nonoxidative CH_4 conversion.

Oxidative CH_4 Conversion

Oxidative coupling of methane (OCM) is another alternative process for CH_4 conversion in the presence of an oxidant, which avoids the formation of coke occurring in NOCM. The primary products by the OCM process are C_2H_6 and C_2H_4, which are formed though Equations 1 and 2.

$$4CH_4 + O_2 \rightarrow 2C_2H_6 + 2H_2O\ (\Delta G^{\circ}_{298\ K} = -320.8\ \text{kJ mol}^{-1}) \qquad \text{(Equation 1)}$$

$$2C_2H_6 + O_2 \rightarrow 2C_2H_4 + 2H_2O\ (\Delta G^{\circ}_{298\ K} = -254.9\ \text{kJ mol}^{-1}) \qquad \text{(Equation 2)}$$

Since it was first reported by Keller and Bhasin in 1982,[13] various metal-oxide catalysts have been extensively studied. Li/MgO catalysts reported by Ito and Lunsford typically exhibit a 38% CH_4 conversion at 993 K along with a 50% C_2 selectivity.[14] However, Li/MgO usually shows poor stability because of the leaching of lithium through volatilization. It is generally accepted that OCM process involves both surface and gas-phase-free radical reactions, which include CH_4 activation to methyl

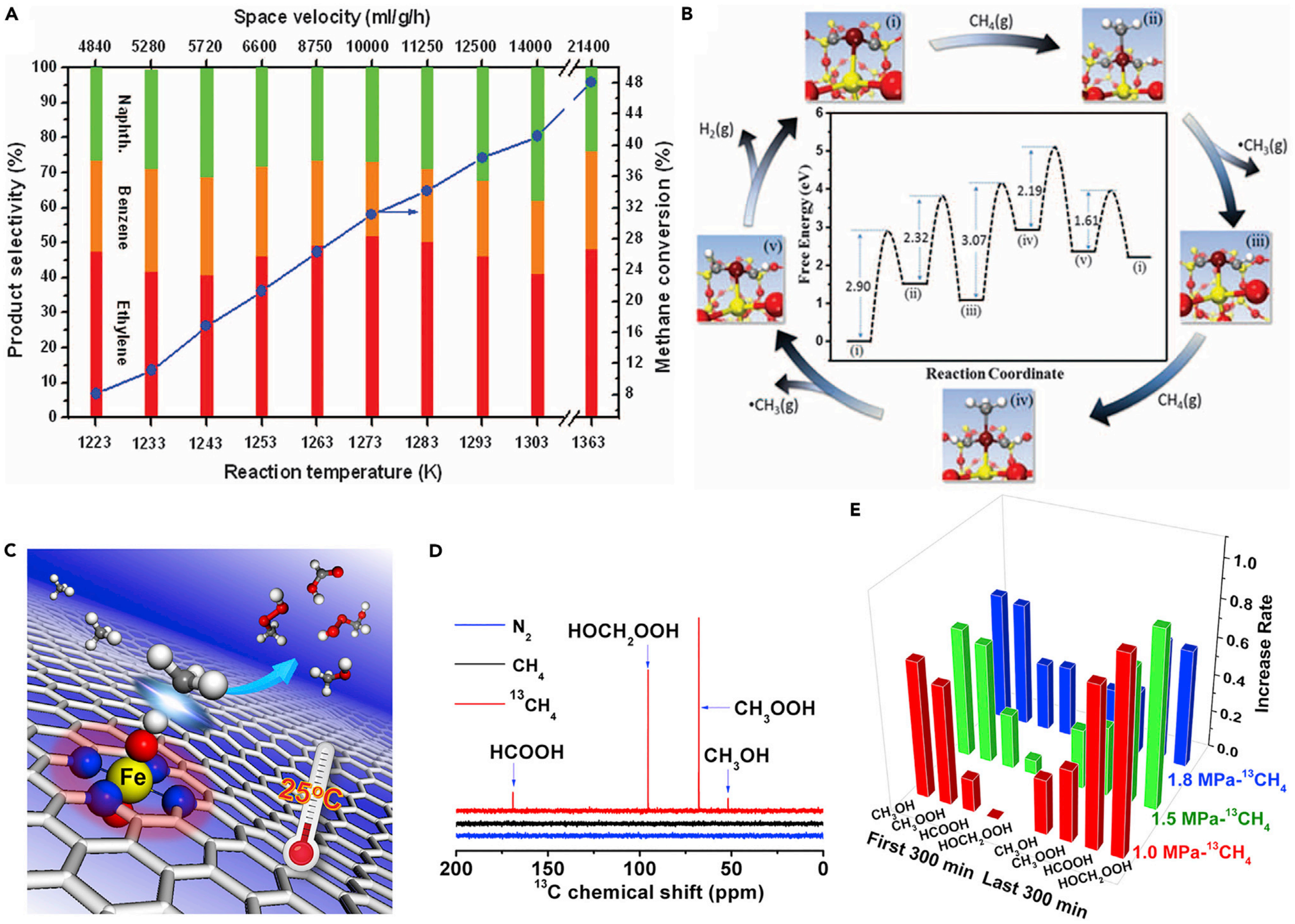

Figure 2. CH_4 Conversion over Fe_1©SiO_2 and Graphene-Confined FeN_4 Catalysts

(A) Catalytic performance of the 0.5% Fe_1©SiO_2. The selectivity of products was denoted as different color bars.

(B) DFT calculations on CH_4 activation at 1,223 K.

(C) Schematic illustration for room-temperature CH_4 conversion over the graphene-confined FeN_4.

(D) ^{13}C NMR spectra of liquid products generated from N_2, CH_4, and $^{13}CH_4$ as a reactant.

(E) Evolution of liquid products for CH_4 conversion under different reaction times and pressures.

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radical (CH_3•) on catalyst surface, gas-phase coupling of two CH_3• species to C_2H_6, and subsequent oxidative dehydrogenation to C_2H_4.[15] At each step, nonselective surface and/or gas-phase oxidation reaction may occur and form CO_x species.

Recently, Baerns et al. made a statistical analysis of the catalysts reported for OCM in 420 literatures from 1982 to 2011 and generated 1,870 datasets on catalyst compositions.[16] Results showed that many of the basic metal-doped oxides exhibit high activity in OCM, giving a 70%–80% C_2 selectivity and with a 15%–27% C_2 yield. The main challenge of OCM lies in the balance of selectivity and conversion because all intermediates or C_2 products are much more reactive than CH_4 in the presence of O_2. They are readily overoxidized into CO_2 under a high CH_4 conversion. In addition to O_2, S_2, SO_3, and NO are used as "softer" oxidants in OCM to improve selectivity, but that cannot avoid complete overoxidation of C_2 products. Despite these obvious issues in OCM process, recent developments by Siluria Technologies seem to be getting closer to the application (http://www.siluria.com).

Partial oxidation methane (POM) is an energy-saving and attractive CH_4 conversion process to valuable oxygenates, such as CH_3OH and CH_3COOH. Nature has demonstrated that methane monooxygenase can activate CH_4 and O_2 to yield CH_3OH under ambient conditions.[17] However, CH_3OH yield by the enzymatic catalysis is quite low because of slow O_2 delivery rate. Recent research indicated that zeolite-based catalysts, such as Cu-ZSM-5 and Cu-MOR, can activate CH_4 and O_2 to form CH_3OH and CH_3COOH at a temperature of $\sim$ 473 K.[18] However, because these oxygenates generated are more likely to undergo oxidation than CH_4, the reaction is typically performed at low CH_4 conversion to prevent overoxidation of the target products.

In addition, recent efforts have also been devoted to the activation of CH_4 in liquid phase with H_2O_2 as oxidant under lower temperatures. Hutchings et al. demonstrated that copper-promoted Fe-ZSM-5 catalyst exhibits high activity for CH_4 conversion utilizing H_2O_2.[19] At a low temperature of 323 K, the selectivity of $CH_3OH > 90\%$ at a 10% CH_4 conversion. This is an energy-saving process for converting CH_4 directly. In the absence of other energy input, however, achieving room-temperature CH_4 conversion will be more fascinating. More recently, Cui et al. discovered that graphene-confined single Fe atoms can be active for CH_4 conversion to C1 oxygenates at room temperature (Figure 2C),[12] giving a 94% selectivity for C1 oxygenates and a 6% conversion of CO_2. Combined with *in operando* time-of-flight mass spectrometry, the ^{13}C NMR experiments, and density functional theory (DFT) calculations, they found that CH_4 is first oxidized to form methyl radical, and then yields CH_3OH and CH_3OOH through combination with hydroxyl and hydroperoxide groups. Subsequently, the resulting CH_3OH is further oxidized to $HOCH_2OOH$ and $HCOOH$ (Figures 2D and 2E). This is a first for $HOCH_2OOH$ to be identified as a product of POM. The utilization of H_2O_2 as an oxidant can indeed decrease reaction temperature for the POM, but the cost of the H_2O_2 is higher than that of the oxidation products. Thus, the *in situ* production of H_2O_2 from H_2, H_2O, or O_2 in reaction systems deserves more attention.

Recently, Bokhoven et al.[20] reported a direct stepwise process for CH_4 conversion using H_2O as oxidant over a Cu-containing zeolite (i.e., the activation of catalyst at 673 K under He flow and subsequent consecutive catalyst exposures to 0.7 MPa CH_4 and then H_2O at 473 K). The CH_3OH productivity attained $\sim$ 0.2 mol per mole of Cu in zeolite at a 97% selectivity.[20] Just recently, Xiao group designed a new hydrophobic modified AuPd/zeolite catalyst for the POM by *in-situ*-generated H_2O_2 from H_2 and O_2.[21] In the reaction system, H_2, O_2, and CH_4 can diffuse into the hydrophobic silanes-coated catalyst active sites, while confining the generated peroxide there to enhance the CH_4 activation probability. The CH_4 conversion reached 17.3% with a CH_3OH selectivity of 92% at 343 K. This work provides a new insight for the direct CH_4 conversion under mild conditions.

In short, the high-temperature activation of CH_4 by the MDA and MTOAH process has been demonstrated to effectively increase CH_4 conversion. However, the limited catalyst lifetime remains a challenge owing to coke deposition by the deep dehydrogenation of CH_4. The development of highly stable catalysts is still required to make these processes more economically viable. Although OCM and POM processes avoid coke formation, oxidative conditions easily lead to CO_2 formation because almost all of intermediates or target products are much more reactive than CH_4 in the presence of oxidant.

CO CONVERSION

CO is a versatile feedstock for the chemical industry and has been manufactured by gasification of coal, biomass, and organic wastes or by reforming methane.[22] The main product of these production processes is syngas, which can be directly used as a chemical raw material to produce clean fuels and value-added chemicals (Figure 1).

FTS to Light Olefins

The FTS is a classical route for syngas conversion to fuels and chemicals that has drawn more attention in recent years due to the shrinking oil resources and growing environmental concerns. It is also an effective process for the synthesis of light olefins ($C_2^=-C_4^=$) from syngas (called Fischer-Tropsch to olefins [FTTO]).[23] The FTS process generally produces a broad distribution of hydrocarbons with different chain lengths because the FTS mechanism involves the hydrogenation of CO on metal surfaces of catalysts to form CH_x ($x < 4$) and then the polymerization of CH_x to higher hydrocarbons.[24] Therefore, the main challenges of FTTO process are to precisely control C−C bond formation and to effectively suppress the C=C bond hydrogenation. Two typical metals, such as Fe and Co, have been widely used in FTS catalysts due to their high activity. Co-based catalysts show high selectivity for long-chain paraffins and are suitable for the manufacture of heavy wax,[25] while relatively inexpensive Fe-based catalysts exhibit high selectivity toward light olefins because of their low activity for the C–C coupling and the hydrogenation of the C=C bond.[26] However, since the limit of Anderson-Schulz-Flory (ASF) distribution in FTS, C_2-C_4 hydrocarbons (include $C_2^=-C_4^=$ olefins and $C_2^\circ-C_4^\circ$ paraffins) selectivity over these catalysts is limited to 58%.[27] It is, therefore, extremely challenging to achieve high selectivity for $C_2^=-C_4^=$ from syngas by FTS.

Recently, de Jong et al. demonstrated that Na and S promoted Fe-based catalysts exhibiting high light-olefin selectivity,[26] giving a 61% $C_2^=-C_4^=$ selectivity and a ~ 22% CH_4 selectivity. The light olefin selectivity exceeds the predicted value by the ASF distribution for the first time. However, achieving simultaneously high $C_2^=-C_4^=$ selectivity and low CH_4 selectivity remains a challenge. More recently, Sun group successfully designed a cobalt carbide (Co_2C) catalyst for the FTTO reaction,[28] affording a 60.8% $C_2^=-C_4^=$ selectivity at a high CO conversion of 31.8%, and the selectivity of CH_4 was reduced to 5%.

Despite the enormous progress that has been achieved in the development of FFTO catalysts, the $C_2^=-C_4^=$ selectivity is still limited to ~ 61% due to the limitation of ASF distribution. It appears, therefore, that to get a higher light-olefin selectivity (> 61%) in FTTO, new reaction processes as well as new catalyst systems must be developed to overcome the inherent restriction from the ASF distribution. In response, Bao et al. recently developed a new oxide-zeolite (OX-ZEO) process that involves the activation of CO and H_2 on a slightly reducible oxide ($ZnCrO_x$) surface and subsequent formation of C−C bond within the confined acidic pores of mesoporous SAPO zeolites (MSAPO).[23] The $C_2^=-C_4^=$ selectivity over the composite catalyst reached 80% at a 17% CO conversion, and the selectivity of CH_4 was 2% (Figure 3A). This light-olefin selectivity is much higher than reported on the Fe- or Co-based catalysts (~ 61%)[26,28] and breaks completely the upper limit of 58% predicted by the ASF model in FTS. Mechanism studies revealed that ketene (CH_2CO) intermediate is first formed from syngas on $ZnCrO_x$ and then converted to olefins on MSAPO. The newly emerging OX-ZEO process for syngas conversion to light olefins attracted much attention when it was reported in 2016 due to the outstanding performances. The same year, Wang et al. reported an integrated process involving CH_3OH synthesis and CH_3OH to olefins for syngas conversion.[29] They found that the $ZnO-ZrO_2$/SAPO-34 catalyst shows high performance for syngas conversion. At a 11% CO conversion, the selectivity of $C_2^=-C_4^=$ reached 74%. Meanwhile, the density of Brønsted acid sites in zeolite plays a vital role in modulating the ratio between olefin and paraffin of C_2—C_4 (Figure 3B).

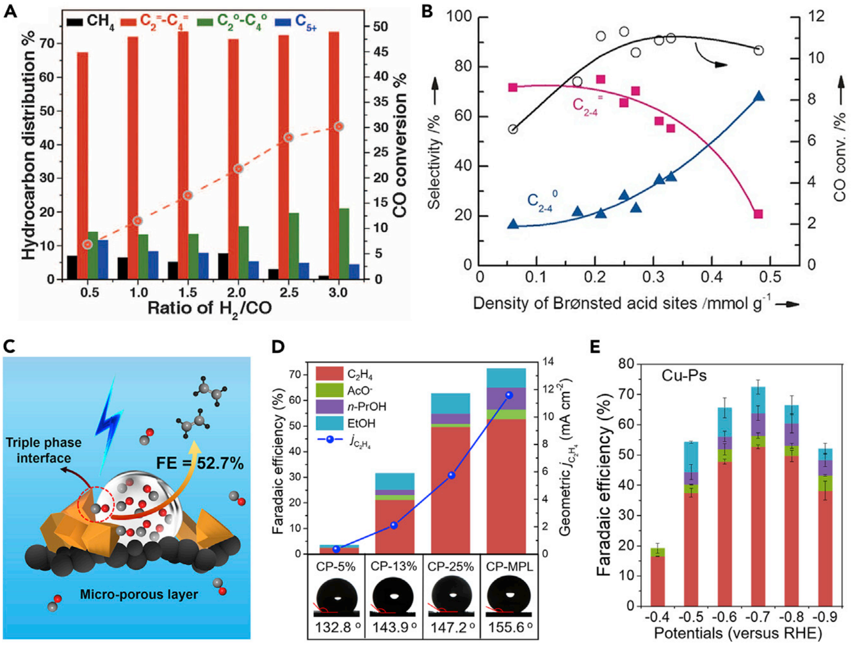

Figure 3. CO Conversion to Light Olefins over Different Catalytic Systems

(A) Catalytic performance of $ZnCrO_x$/MSAPO catalyst for syngas conversion. Reaction condition: 673 K, 2.5 MPa, 4,800 mL g_{cat}^{-1} h^{-1}. Reprinted with permission from Jiao et al.[23] Copyright 2016 Springer AAAS.

(B) Effect of the density of Brønsted acid sites on the catalytic performance of ZnO-ZrO_2/SAPO-34 for syngas conversion (673 K, 1MPa, 3,600 mL g_{cat}^{-1} h^{-1}, H_2/CO = 2:1). Reprinted with permission from Cheng et al.[29] Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA.

(C) Schematic illustration for ECOTE process on Cu catalysts.

(D) Effect of the hydrophobicity of carbon paper (CP) on the performance of Cu/CP for ECOTE at 298 K in 1 M of KOH.

(E) Applied potentials effect on the performance of ECOTE. Reaction condition: 1 M KOH, 298 K. (C–E) were reprinted with permission from Chen et al.[30] Copyright 2020 Wiley-VCH Verlag GmbH & Co. KGaA.

Based on the OX-ZEO process,[23] in September 2019, the world's first FTTO pilot-scale unit was successfully constructed and started up in Yulin, Shaanxi by the Dalian Institute of Chemical Physics (DICP), collaborating with Shaanxi Yanchang Petroleum(Group). In the pilot-scale unit, the selectivity toward $C_2^{=}$–$C_4^{=}$ exceeded 75%, and the CO single-pass conversion was higher than 50%.[31,32] The success of this pilot-scale test not only further verifies the advancement and feasibility of the OX-ZEO process for FTTO but also speeds up the industrialization process of this technology.

For the FTTO, however, the process typically suffers from harsh temperature and pressure conditions. Meanwhile, the products from the FTTO contain 30%–50% CO_2 selectivity, which causes carbon loss and, thus, decreases carbon mole selectivity for light olefins. In addition, the resulting gas mixture containing C_1–C_4 hydrocarbons needs additional separation process so as to obtain high-purity olefins such as $C_2^{=}$ and $C_3^{=}$. Thus, the development of low-energy and highly selective CO conversion process for light-olefin synthesis is still required.

ECOTE has drawn much attention because the process is more economical and eco-friendly than FTTO. Jiao group designed a three-compartment CO flow electrolyzer for CO reduction, achieving a ~ 91% faradic efficiency (FE) for C_{2+} products and with a ~ 40% FE of C_2H_4.[33,34] Recently, Ripatti et al. constructed a CO gas diffusion electrolysis cell for efficient CO electrolysis by carefully controlling gas and ion transport.[35] The total FE of CO attained 72% at a 144 mA cm^{-2} current density with a 43% FE for C_2H_4. More recently, Chen et al. reported an efficient room-temperature electrocatalytic process for ECOTE (Figures 3C–3E) using H_2O as hydrogen resources over Cu catalyst, achieving as high as 52.7% FE for C_2H_4.[30] Meanwhile, almost without other carbon-based gaseous products, such as C_1–C_4 hydrocarbons, CO_2 was formed by the ECOTE process. The carbon mole selectivity for C_2H_4 attained ~70%, breaking though the limitation of 30% selectivity toward C_2 hydrocarbons in FTS, which usually delivers an uncontrollable mixture of C_1–C_4 hydrocarbons and massive CO_2. During the same period, Sinton and coworkers reported that constraining CO coverage on Cu surface can promote C_2H_4 production, giving a ~70% FE for C_2H_4 and a >800 mA cm^{-2} partial current density.[36]

Compared with the thermo-catalytic CO hydrogenation, the electrocatalytic CO reduction shows a completely different mechanism. In a thermo-catalytic process, many researchers believe that CO first reacts with H_2 to form CH_x* intermediates and then occurs a chain growth via C–C coupling.[23,37] For the electric-catalytic process, two adsorbed CO* usually reacted with H_2O to yield C_2 oxygen-containing intermediates and then hydrogenation to CCH*, which is further converted to C_2H_4. CHCOH* has been identified as a key oxygen-containing group for C_2H_4 formation. DFT calculations indicated that limited coverage CO on catalyst surface will promote C_2H_4 production.[34,30,36]

WGS for H_2 Production

The WGS reaction ($CO + H_2O \rightarrow CO_2 + H_2$) is a very important process for H_2 production and CO removal in chemical industry, which has extensively been studied in the past few decades. The reaction is reversible and mildly exothermic (~41 kJ mol^{-1}), therefore, the equilibrium can be moved toward H_2 production at low temperatures while higher temperatures will favor the reaction kinetics. In the industry, the WGS reaction is usually performed in a two-stage technology, including a high-temperature (583–773 K) WGS (HT-WGS) over a Fe_2O_3-Cr_2O_3 catalyst for enhancing reaction rate,[38] followed by a low temperature (473–523 K) WGS (LT-WGS) over a Cu/ZnO/Al_2O_3 catalyst to achieve low CO levels.[39] Despite the technology being acceptable on an industrial scale, it is often considered an unsatisfactory process because of the high energy consumption and the limited CO removal capability (the amount of CO residuals is 0.1%–0.3%). It is reported that the Pt catalyst used in hydrogen fuel cells is poisoned by the traces amounts of CO (~100 ppm) in H_2.[40] Thus, the development of an effective single-stage LT-WGS process for high-purity H_2 production is a highly desirable but challenging task, which requires innovative catalytic materials and reaction processes. Pt-based catalysts are considered promising WGS catalysts because of their high low-temperature activity, especially when Pt dispersed on metal oxides with oxygen vacancies, such as CeO_2 and doped-CeO_2 supports.[41,42] Recently, a bifunctional mechanism of ceria-supported Pt catalysts has been inferred in a review by Flytzani-Stephanopoulos et al.,[43] in which ceria dissociate H_2O to form OH* and H* when CO is adsorbed on the Pt surface, and then adsorbed CO reacts with OH* to yield CO_2. In the real world practice, however, ceria itself is susceptible to deactivation because of the formation of surface $Ce(OH)CO_3$ under low temperature.

Recently, Flytzani-Stephanopoulos et al. found that dispersing mononuclear gold onto alkali (e.g., Na and K) promoted inert supports such as KLTL-zeolite, and mesoporous MCM-41 silica can be active for the WGS reaction (Figure 4A),[44] which makes an oxide support with oxygen vacancies no longer a requirement. More recently, Ma and coworkers developed an efficient catalyst for the LT-WGS reaction

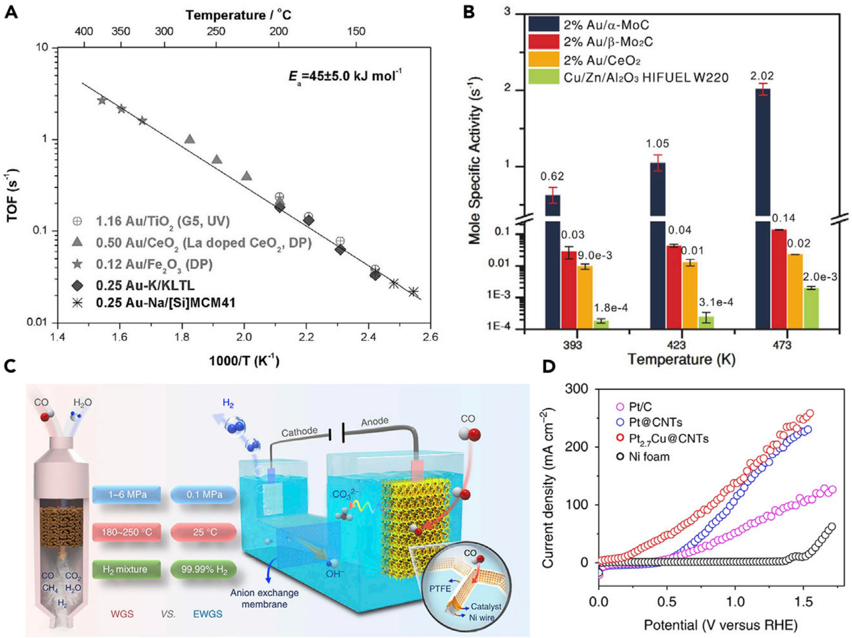

Figure 4. The WGS and RT-EWGS Process in Different Catalytic Systems

(A) Turnover frequency plot of different catalysts for the WGS reaction. Reprinted with permission from Yang et al.[44] Copyright 2014 Springer AAAS.

(B) Catalytic performance of different catalysts for the WGS reaction. Reprinted with permission from Yao et al.[45] Copyright 2017 Springer AAAS.

(C) Schematic illustration for the traditional WGS and EWGS process.

(D) Catalytic performance of different catalysts for the EWGS reaction.

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by the dispersion of atomic-layered Au clusters onto α-MoC substrate (Au/α-MoC).[45] α-MoC activates H_2O, forming the surface hydroxyl groups, whereas CO adsorbed on Au sites react with the surface hydroxyl groups. At a low temperature of <423 K, the Au/α-MoC displayed 10 times more activity than the previous catalysts (~ 0.1 $mol_{CO}\ mol_{metal}^{-1}\ s^{-1}$) for the LT-WGS (Figure 4B). The Au/α-MoC has great application potential in small-scale H_2-generation devices.

For the WGS, however, H_2 produced by the thermal-driven process typically contains appreciable amounts of CO_2, together with a small number of CO and CH_4, which needs additional separation process so as to obtain high-purity H_2. Recently, some new catalytic processes have been developed to circumvent the aforementioned issues through the use of electrical energy, such as the EWGS route. The process decoupling the WGS reaction into two separate processes, including cathodic H_2O reduction to H_2 and anodic CO oxidation to CO_2, in an electrolytic cell.[47] More recently, Deng group developed an efficient room-temperature EWGS (RT-EWGS) process for direct H_2 production through Equations 3, 4, and 5.[46]

$$\text{Anode: } CO + 4OH— \rightarrow CO_3^{2-} + 2H_2O + 2e^- \qquad \text{(Equation 3)}$$

$$\text{Cathode: } 2H_2O + 2e^- \rightarrow H_2 + 2OH— \qquad \text{(Equation 4)}$$

$$\text{Total: } CO + 2OH— \rightarrow H_2 + CO_3^{2-} \qquad \text{(Equation 5)}$$

The RT-EWGS process offered a ∼100% FE and a >99.99% high-purity H_2 without the separation and purification steps (Figures 4C and 4D). Though designing and optimizing the anode catalytic system, anodic onset potential was reduced to ∼0 V with a 70 mA cm^{-2} current density at 0.6 V. DFT calculations indicated the adsorbed CO (CO*) on Pt surfaces reacts either with OH^- or OH* through associative mechanisms (via COOH*) or with O* through a redox mechanism, leading to the formation of CO_2. The novel RT-EWGS process significantly overcomes the problems encountered in the traditional WGS reaction, which provides a new strategy for high-purity H_2 production under mild conditions.

In short, CO conversions have achieved an important advancement in recent years. The OX-ZEO process for syngas conversion shows good prospects for industrial application. The current main challenge of this process is to suppress CO_2 formation. In addition, the ECOTE process can also be a potentially interesting option owing to its high carbon molar selectivity toward C_2H_4, low energy consumption, and near-zero CO_2 emission. For WGS reaction, Au/α-MoC catalyst reported by the Ma group displays good catalytic performance in the LT-WGS reaction. Meanwhile, the new RT-EWGS process provides a new strategy for high-purity H_2 production from CO and H_2O. However, further efforts are still needed for the design and synthesis of non-noble-metal catalysts with high catalytic performance for the LT-WGS or RT-EWGS reaction.

CH_3OH CONVERSION

CH_3OH, which is mainly produced by syngas conversion, is an important C1-chemistry platform for the production of high-value-added chemicals (Figure 1) and has also been directly used as an additive for gasoline or an alternative fuel for fuel cells.[48] Furthermore, CH_3OH also represents a promising hydrogen storage system because of its low cost and high hydrogen content (12.6 wt %).

MSR for H_2 Production

The MSR for H_2 production ($CH_3OH + H_2O \rightarrow CO_2 + 3H_2$) is an important application in the background of methanol-based hydrogen storage systems. So far, there have been numerous studies showing that the main challenge of MSR lies in suppressing CO formation and increasing catalyst stability. Cu/ZnO catalysts are often used for MSR owing to their high activity and low cost.[49] However, with the increase of running time, the catalysts gradually deactivate ascribed to the sintering of Cu particles. Alejo et al. indicated that the introduction of alumina into Cu/ZnO can enhance the catalytic stability and inhibition of CO formation in MSR,[50] despite slightly reducing the CH_3OH conversion rate. Recently, Gao et al. discovered that Cu-Al spinel oxide ($CuAl_2O_4$) exhibits higher activity than the commercial Cu/ZnO/Al_2O_3 catalyst for MSR,[51] and they found that MSR can be initiated over the CuO phase at a lower temperature, and then active Cu are gradually released from $CuAl_2O_4$. It is interesting to note that the catalyst requires no prereduction treatment, which not only eliminates the Cu sintering during the catalyst reduction but also efficiently alleviates the Cu particles' sintering rate during MSR reaction.

Besides the Cu catalysts, noble-metal catalysts have been drawing more and more attention due to their high low-temperature activity. Dumesic et al. exhibited that H_2 can be produced over a Pt/Al_2O_3 by the MSR process at temperatures of 473–498 K.[52] To further decrease the reaction temperature and the maximization of Pt utilization, Ma group developed a bifunctional Pt_1/α-MoC single-atom catalyst.[53] The atomically dispersed Pt over α-MoC maximally exposes the active interface of the catalyst and effectively increases the density of active sites for the MSR. Meanwhile, the α-MoC provides highly active sites for H_2O dissociation, producing abundant surface hydroxyls that accelerate the MSR reaction on catalyst interface. At low temperatures of 423–463 K, the Pt_1/α-MoC exhibited an average turnover frequency of 18,046 moles of hydrogen per mole of Pt per hour and a <0.1% CO selectivity. This reliable catalyst paves the way for the advancement of CH_3OH-based hydrogen storage systems.

Conversion of Methanol to C_{2+} Products

Direct CH_3OH conversion to value-added chemicals though the C–C coupling reaction is an attractive but challenging reaction. The current primary method for CH_3OH conversion involving C−C bond formation is based on dehydrative oligomerization processes, such as methanol to olefins (MTO) and methanol to aromatics (MTA).[54] Among them, the MTO process represents a key future technology for light olefin production from coal or natural gas owing to the rapidly increasing demand for olefins. Since it was first reported by Mobil Corporation in 1977,[55] a series of important processes have been made in the catalyst preparation, process engineering, and reaction mechanism.[56]

CH_3OH is a highly active molecule and, therefore, very sensitive to the catalyst. It has been indicated that the products are diverse over different zeolite catalysts for the MTO reaction. Currently, the most commonly used catalysts for the MTO reaction are acidic zeolite catalysts and the main products are $C_2^=$ and $C_3^=$.[54] In 2010, a world's first MTO unit was successfully started up by the DICP, which is thought of as a significant milestone and key step for the production of light olefins from coal or natural gas.[57] Recently, Liu group briefly summarized the key issues for MTO technology from fundamentals to commercialization.[57] However, since the reaction system of MTO is very complicated, a thorough understanding of the CH_3OH activation and the C−C bond formation remains a challenge. For more details on the MTO reaction, readers are suggested to read more specialized reviews reported by Liu et al.[56,57] and Gascon et al.[54]

In addition to the production of light olefins, CH_3OH can also be converted to high-value-added ethylene glycol (EG) and hydrogen by the direct C−C coupling reaction through Equation 6, which is a dream reaction with atomic economy.

$$2CH_3OH \rightarrow HOCH_2CH_2OH + H_2 \qquad \text{(Equation 6)}$$

However, this reaction is very difficult to achieve by thermal catalysis process because CH_3OH is a high reactivity molecule and is easily to be oxidized to CH_2O and HCOOH, the selective activation of C–H bond without affecting hydroxyl group in CH_3OH is an extremely challenging task. To date, no suitable catalytic route in conversion of methanol to EG (MTEG) via a thermo-catalytic process has been discovered.

Photocatalytic process is an attractive alternative technology to realize the direct conversion of CH_3OH to EG by the C—C coupling reaction. In 1994, Yanagida et al. found that ZnS semiconductor is active for photocatalytic conversion of the CH_3OH solution to EG and H_2 by UV irradiation, giving a 2% of CH_3OH conversion.[58] Subsequently, Gu et al. adopted freshly prepared colloidal ZnS to catalyze the reaction by UV irradiation, CH_3OH conversion was increased to ∼20% and obtained >90% selectivity for EG.[59] Recently, Xie et al. reported that MoS_2-modified CdS catalyst can catalyze conversion of CH_3OH to EG by a visible-light-driven

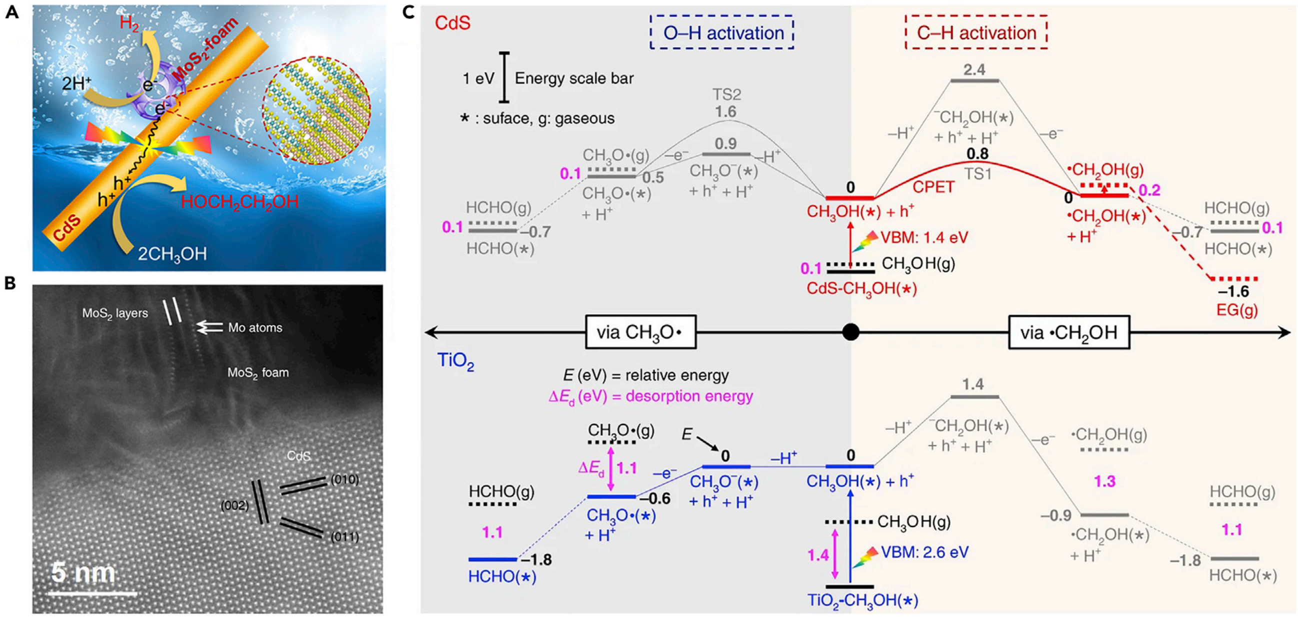

Figure 5. MTEG Process and Reaction Mechanism on MoS_2 Foam/CdS Catalyst

(A) Schematic illustration for MTEG process over the MoS_2 foam/CdS catalyst.

(B) TEM image of MoS_2 foam/CdS catalyst.

(C) Reaction energy profiles for CH_3OH conversion over CdS and TiO_2.

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dehydrogenative process (Figures 5A and 5B), giving a 90% EG selectivity and with a 16% EG yield.[60] DFT calculations and *in situ* electron spin resonance (ESR) spectroscopic studies have shown that the uniqueness of the catalyst lies in the selective cleaving of the C—H bond instead of C—O and O—H bonds in CH_3OH via a radical mechanism to form $\bullet CH_2OH$ species and then coupling to yield EG (Figure 5C). On the conventional TiO_2 surfaces, the O–H bond of hydroxyl group in CH_3OH is more likely to cleave and form the $CH_3O\bullet$ species, which leads to the formation of HCHO. This work not only presents a new strategy for direct CH_3OH conversion to EG but also develops an efficient way to selectively activate C—H bond without affecting hydroxyl group in the same alcohol molecule. If the production scale can be further increased, the visible-light-driven MTEG will be a very attractive process.

In short, some important progresses have been made for CH_3OH conversion in recent years. For the MRS reaction, the benchmark catalysts are Cu- and Pt-based catalysts. The Pt_1/α-MoC catalyst reported by the Ma group exhibits high LT-MRS activity. The search for non-noble-metal catalysts with high activity and low CO selectivity has become a critical issue in the LT-MSR research field. Furthermore, the conversion of CH_3OH to C_{2+} products by MTO and MTEG processes remains one of the most active research fields in the future because the demand for light olefins and EG will be increasing continuously.

CO_2 CONVERSION

Hydrogenation of CO_2 by the renewable hydrogen, which was produced from water and clean electricity (Figure 1), into valuable chemicals is an effective solution to alleviate carbon emissions and achieve carbon resource utilization. However, the high stability of the CO_2 molecule ($\Delta G°_{298\ K} = -396$ kJ mol^{-1}) leads to low reaction conversions and poor product selectivities in CO_2 hydrogenation. Although it is challenging, great progress has been made in hydrogenation of CO_2 to C_1 products, such as CO, HCOOH, and CH_3OH. Among them, hydrogenation to CH_3OH is one of the most attractive research topics because of the wide application of CH_3OH as mentioned above.

Currently, industrial-scale CO_2 hydrogenation to CH_3OH is realized by conversion of mixed gas (CO, H_2, and CO_2) over a $Cu/ZnO/Al_2O_3$ catalyst.[61] Similarly, Cu-based catalysts can also catalyze hydrogenation of sole CO_2 to CH_3OH. Recent publications have demonstrated that Cu/ZnO catalysts exhibit a 30%–70% CH_3OH selectivity and with a <30% conversion under 493–573 K, < 5 MPa and the initial H_2/CO_2 molar ratio is 3.[62] By changing the reaction conditions (P = 36 MPa, H_2/CO_2 = 10), CH_3OH selectivity over a $Cu/ZnO/Al_2O_3$ catalyst can be reached 98% at a 95% CO_2 conversion. In addition to Cu, noble-metal (e.g., In, Au, Pt, Pd, etc.) materials exhibited high activity for CO_2 hydrogenation to CH_3OH. For example, In_2O_3/ZrO_2 catalysts showed close to a 100% CH_3OH selectivity at a 5% CO_2 conversion. Recently, Li et al. found $ZnO–ZrO_2$ solid solution exhibits a high activity for CO_2 hydrogenation, giving a 86%–91% CH_3OH selectivity and a >10% CO_2 conversion. The reaction mechanism of CH_3OH synthesis is generally classified into two categories. The first mechanism involves the hydrogenation of HCOO* species to produce formate intermediates. The second mechanism involves the dissociation of HOCO* species to form CO* intermediates. The rate-determining step for CO_2 hydrogenation to CH_3OH is usually the activation of CO_2, which involves CO_2 chemisorption on the catalyst surface and subsequent electron transfer from the catalyst into CO_2.

In addition to CH_3OH, several important advances have also been achieved in CO_2 hydrogenation to C_{2+} products, such as light olefins and aromatics, despite that it is more challenging than synthesis of CH_3OH due to the high barrier for the coupling of C–C. The conventional pathway for CO_2 hydrogenation to light olefins mainly involves the hydrogenation of CO_2 to CO by the reverse water-gas shift (RWGS) reaction and then hydrogenation to light olefins though FTS.[63] Currently, much research is focused on using FTS catalysts with some modifications, but these catalysts typically have low $C_2^=–C_4^=$ selectivity due to the limit of ASF distribution in FTS. Song et al. recently reported that the K-promoted Fe-Co-Zr polymetallic fibers demonstrated a 27.5% light olefins selectivity.[64] Afterward, Davis et al. found that the introduction of Rb into iron oxalate can potentially facilitate the dissociation of C–O bond while suppressing hydrogen coverage, leading to enhance $C_2^=–C_4^=$ selectivity (~35%).[65] So far, the reaction mechanism for CO_2 to light olefins remains controversial, despite some advances that have been made. For RWGS reaction, the formation of CO* species either though the decomposition of HOCO* or direct dissociation of C–O bond in CO_2*. For subsequent FTS process, many of the researchers believe that light olefin formation involves CO* reaction with hydrogen to form product CH_x* intermediates and then a chain growth via C–C coupling.

In addition to the FTS process, tandem catalysts have been extensively studied for CO_2 hydrogenation through a CH_3OH-mediated route. Li group recently reported that the combination of a $ZnZrO_x$ with SAPO-34 shows an excellent light-olefin selectivity.[66] $C_2^=–C_4^=$ selectivity reached 80% among hydrocarbon products at a 12.6% CO_2 conversion at 653 K, and the selectivity for CO byproduct was 47%. The authors claimed that CO_2 was first hydrogenated on ZnZrOx and formed CH_xO, and then CH_xO species were converted to light olefins on SAPO-34. Recently, Sun et al. found that the combination of In-Zr oxide with SAPO-34 shows a superior activity with a 35.5% CO_2 conversion at a $C_2^=–C_4^=$ selectivity of 76.4% at 673 K, but the selectivity of CO was elevated to 80%.[67] Besides light olefins, high valuable aromatics can also be produced by the similar strategy via integrating hydrogenation of CO_2 to CH_3OH/DME and CH_3OH/DME to aromatics. Liu group recently found that $ZnAlO_x$/H-ZSM-5 catalyst exhibits high catalytic performance for CO_2 hydrogenation,[68] the selectivity (excluded CO) of aromatics attained 73.9% at a 9.1% CO_2 conversion, and the CO selectivity was 57.4%. More recently, Li group reported that ZnZrO/ZSM-5 catalyst can catalyze CO_2 hydrogenation with a 73% aromatics selectivity and with a 14% CO_2 conversion, and the selectivity of CO was decreased to 44%. Meanwhile, it has been clearly indicated that there is a synergistic effect between these two catalysts.[69] In a word, the tandem catalysts can indeed improve olefins or aromatics selectivity in CO_2 hydrogenation; however, achieving high selectivity toward target products while suppressing CO formation remains a challenge.

The electrocatalytic CO_2 reduction reaction (CO_2RR) using renewable electrical energy is another alternative and prospective process for CO_2 conversion because of its mild operating conditions using water as the reductant instead of hydrogen. Over the past few decades, great progress has been achieved in the design and preparation of high-performance catalysts for the orientable synthesis of different reductive products, such as CO, C_2H_4, CH_3CH_2OH, etc. For example, metal-containing nitrogen-doped carbon (Metal-N-C) catalysts have shown high selectivity for the CO_2 reduction to CO.[70] However, although great advances have been made, there are some inevitable issues including the low reaction rate, limited energy efficiency, and difficult selectivity control requiring to be resolved for CO_2RR.

In short, taking advantage of greenhouse gas CO_2 as raw material for producing valuable chemicals has dawn a lot of attention. The direct CO_2 hydrogenation over the tandem catalysts via a CH_3OH-mediated process is a promising strategy for the synthesis of light olefins or aromatics. The current main challenge of this process is to improve CO_2 conversion and avoid the undesirable CO byproducts. Thus, the design of new catalysts and development of new reaction processes are still desperately needed for the hydrogenation of CO_2 to the hydrocarbon products. The electrocatalytic CO_2RR is another alternative strategy for CO_2 conversion. However, due to the low energy efficiency, low selectivity toward a single product, and low catalytic stability, further efforts are still needed to overcome these issues, which need innovative catalytic materials and reaction processes.

SUMMARIES AND PERSPECTIVES

Catalytic conversion of C1 molecules to fuels and value-added chemicals is an important research area in chemical industry that receives great attention from both academia and industry. Although much progress has been made already, there are a number of scientific and technological issues yet to be solved, as discussed in the following.

CH_4 conversion should be currently the most challenging process in C1 chemistry due to its chemical inertness. For the NOCM and MDA processes, one of the most key issues is the limited lifetime of catalysts due to coke formation under high reaction temperatures. A breakthrough in MTOAH was reported by Bao et al. that CH_4 was selectively converted to C_2H_4, aromatics and H_2 over a highly thermostable Fe_1©SiO_2 catalyst at 1,363 K. More significantly, no coke was formed over the catalyst and, thus, extending catalyst lifetimes (>60 h). This MTOAH process is a fascinating atom-economy of CH_4 conversion strategy and will inspire research interests of both academia and chemical industry in the future. New efforts should be aimed to elucidate the active sites and mechanism of the catalytic reaction in some advanced catalysts (e.g., single-atom catalysts and zeolite-based catalysts) by utilizing theoretical calculations and the development of *in situ* and *operando* characterization techniques. This would provide important guidance for the development of high-performance next-generation catalysts for CH_4 nonoxidative conversion. Just recently, Li et al. found a new quasi-Mars-van-Krevelen surface reaction mechanism involving extracting and refilling the surface carbon atoms for the NOCM on Fe_1©SiO_2 catalyst by comprehensive computational modeling and simulations.[71] In addition to these nonoxidative CH_4 conversion processes, the POM is also a very attractive process, avoiding coke formation. However, all intermediates or products are much more reactive than CH_4 in the presence of oxidant, leading to formidable challenges in the balance of selectivity and conversion for POM. There are some suggestions for the direct CH_4 conversion as follows. (1) The development of new pathway and new reaction. For example, the cross-coupling of CH_4 with other hydrocarbon compounds, such as ethylene, benzene, and naphthalene, to yield methylation products. (2) The rationally designed catalyst with high activity for oriented conversion of CH_4. Two-dimensional (2D) materials (e.g., MoS_2, grapheme, and Mxene) might be good candidates, due to their unique electronic properties and high specific surface areas. (3) Using O_2 or air instead of H_2O_2, S_2, NO, and other high-cost reactants for activation of CH_4. (4) The introduction of external energy, such as light, electricity, and plasma, and development of multi-energy coupled modes for CH_4 conversion.

Syngas conversion and CO_2 hydrogenation to C_{2+} hydrocarbon products are very attractive research topics in C1 chemistry. However, since their products in both of these reactions usually follow the ASF distribution, achieving a high selectivity toward a specific product is very difficult. For syngas conversion, iron-based catalysts could be a good choice for the conversion of syngas into light olefins, due to its inexpensive, high selectivity and its potential for achieving a lower CH_4 selectivity than the prediction value by the ASF model in FTS. In addition, the OX-ZEO process exhibits good prospects for industrial application in syngas conversion due to its unparalleled selectivity toward light olefins. For CO_2 conversion, bifunctional metal oxide/zeolite catalysts could be a potential choice for the hydrogenation of CO_2 to light olefins or aromatics, which significantly break the ASF distribution. So far, despite the bifunctional metal oxide/zeolite catalysts exhibiting high C_{2+} product selectivities in syngas conversion or CO_2 hydrogenation, some challenges still remain. One significant issue is the occurrence of kinetically favorable WGS and RWGS reaction at a high reaction temperature, leading to the production CO_2 and CO during the conversion of CO and the hydrogenation of CO_2, respectively. In addition, the bifunctional catalysts typically show lower catalytic activity than FTS or modified FTS catalysts for the conversion of CO or CO_2. Future research should focus on (1) precise identification of the structural evolution of these high-performance catalysts (e.g., iron-based catalysts and bifunctional metal oxide/zeolite catalysts), deep understanding of the properties of the true catalytically active centers, and monitoring of real-time reaction products during syngas conversion or CO_2 hydrogenation by means of *in situ* and *operando* characterization techniques, such as environment scanning electron microscope, synchrotron radiation-based X-ray spectrum, to rational design a catalyst that can suppress CO_2 and CO formation during catalytic syngas conversion and CO_2 hydrogenation, respectively. (2) Development of new catalyst synthesis strategies. For example, the synthesis of bifunctional catalysts (e.g., metals, metal oxides, or metal carbides/zeolites) with designable and tunable structures by a 3D printing technology assisted with artificial intelligence (AI), which has been used in preparing high-performance catalysts for CH_4 combustion and syngas methanation.[72,73]

Hydrogen is a clean energy source, and the production and storage of hydrogen is a research hotspot in the field of hydrogen energy utilization. The WGS reaction for large-scale hydrogen production continues to be a very important process. Supported noble-metal (e.g., Au and Pt)-based catalysts have shown high activity in LT-WGS reaction due to the synergetic effect that occurred at the interface of metals and support. Unfortunately, their large-scale applications are limited by the high price and low reserve of noble metals. Future studies should focus more on the design and development of non-noble-metal LT-WGS catalysts with desired properties and efficiency. Confined transition-metal single-atom catalysts and clusters could be a potential alternative for LT-WGS. In particular, confined single-atom catalysts could offer abundant interfacial active sites to promote H_2O dissociation and CO activation at a low reaction temperature and finally improve LT-WGS activity. Similarly, for the MSR process, the search for non-noble-metal catalysts is always a critical issue. The emerging $CuAlO_4$ catalysts are very promising catalysts in MSR due to their high activity at low temperatures, but the formation of CO caused by CH_3OH pyrolysis and/or RWGS reaction and the deactivation of catalysts caused by thermal sintering remain challenging. Meanwhile, the true coordination environment of active surface Cu in during MSR is still ambiguity. New efforts toward an in-depth insight into the exact nature and structure of catalysts are required to obtain superior MSR catalysts.

Generally, these thermal-driven C1 molecule conversions require high temperatures and pressures, and conversions and the selectivities of products are controlled by the thermodynamics or kinetics. In contrast, the electro- and light-driven C1-molecule conversion processes can be performed under mild conditions, and there are many conversion processes that have been developed for C1 chemistry. For example, visible-light-driven coupling of CH_3OH into EG, the RT-EWGS process for the direct production of high-purity H_2, the electrocatalytic CO or CO_2 reduction using H_2O as the reductant to yield light olefins and CO, respectively. However, from the point of scaleup, how to achieve high yield toward a single product at high energy efficiency remains a great challenge. New efforts should focus on optimizing the performance of catalysts at each C1 conversion process and developing of new pathway and new reaction by electro- or photo-catalysis.

In summary, the catalytic conversion of C1 molecules into fuels and value-added chemicals is currently attracting great attention from both academia and industry, and the research interests in the area is expected to continually grow in the future because of the increasing need for the manufacture of clean fuels and petrochemical commodities. However, due to the C1 molecules existing either in the relatively inert nature or having high reactivity, the selectivity control, energy saving, and emission reduction remain great challenges for C1 chemistry. Some newly emerging processes, such as MTOAH, OX-ZEO, EWGS, ECOTE, and MTEG, provide important guidance and reference to the development of catalytic processes for C1 chemistry. Finally, the development of mild-condition C1 molecule conversion technologies will become increasingly vital and imperative with the increment of social concern toward the issues of energy and environment.

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AUTHOR CONTRIBUTIONS

D.D. and X.B. proposed the topic of the perspective and revised the manuscript, and Y.L., D.D., and X.B. wrote the manuscript.

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