Design and tailoring of advanced catalytic process for light alkanes upgrading

Wenyao Chen | Xuezhi Duan | Xinggui Zhou | De Chen

1State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai, China
2Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim, Norway

Abstract

The wide and huge reservation of shale gas around the world has drastically altered the global energy and chemicals market, boosting the productions of hydrocarbons and their derivatives by providing massive light alkanes at low cost. Direct conversion of alkanes into the value-added chemicals remains energy-intensive and requires harsh reaction conditions due to its ultrahigh C–H bond strength. Hence, the quest of alternative reaction pathway for alkane conversion into target product with high yield under mild conditions for a long-term operation emerges as the key technique of shale gas utilization. In this review, we summarize important progresses in the catalytic conversions of light alkanes with emphases on the design and preparation of novel heterogeneous catalysts, as well as the development of advanced processes in the recent 10 years. The perspectives of potential areas for future study are also provided.

KEYWORDS
advanced processes, alkane conversion, C–H bond activation, novel heterogeneous catalysts, yield and stability

1 | INTRODUCTION

The anticipated depletion of petroleum reserves coupled with the increasingly serious environmental problems has triggered a worldwide interest for the quest of alternative resources and development of efficient conversion processes. With the large-scale exploitation of shale gas in the United States, it has been regarded as a potential game-changer to the global energy market, whose boom has spread out to Europe and China quickly. Typically, shale gas is constituted by alkane, mainly methane with substantial amounts of ethane and propane, in addition to a small fraction of inorganic gases, including carbon dioxide, nitrogen, and hydrogen sulfide. The conventional route to utilize these light alkanes, especially methane, is direct burning in various combustion processes, releasing amounts of greenhouse gas to the atmosphere. On the other hand, because most of shale gas are reserved in depopulated areas and their lower boiling points, the transportation and storage of shale gas are energy intensive and economically inviable. Therefore, it remains a critical yet formidable challenge for...
economic and environmental-friendly conversions of shale gas, mainly light chain alkane, into transportable and value-added chemical products.

In light of the high C–H bond energy in methane (H–CH$_3$, 439.6 kJ mol$^{-1}$), ethane (H–CH$_2$CH$_3$, 423.3 kJ mol$^{-1}$), and propane (H–CH$_2$CH$_2$CH$_3$, 422.2 kJ mol$^{-1}$/H–CH(CH$_3$)$_2$, 409.2 kJ mol$^{-1}$), the activations of these light alkane are usually conducted under high temperature and pressure, which has been suggested as the “holy grail” in catalysis. Taking the main component of methane, for example, its current industrial utilization is based on an indirect route, proceeding by catalytic steam reforming to syngas and subsequent Fischer-Tropsch synthesis to hydrocarbon. During this process, the high endothermic enthalpy ($\Delta H^0$ 298 K = +206.2 kJ mol$^{-1}$) renders the steam reforming highly energy consumptive, which is usually operated under much high temperature of 700°C to 1000°C. In addition to these drawbacks, the indirect route incorporates the addition of oxygen atoms into carbon atoms to form syngas followed by the removal of oxygen atoms to produce hydrocarbon. As a result, the addition and removal of oxygen would further increase the operation cost, and the resultant CO$_2$ production significantly lowers the carbon atom utilization efficiency. In these regards, reducing the operation temperature and pressure while maintaining the high activity and selectivity to target products are highly desirable to reduce the investment and operation costs, and alleviate the environment and energy problems.

As an alternative to the indirect conversion of light alkane, the direct conversion without undergoing the intermediate step of syngas production has aroused considerable attention from the chemists over decades, which could be further categorized into the homogeneous and heterogeneous pathways. Although providing high yield of target product, the practical application of homogeneous systems is still hampered by the harsh reaction conditions in most cases, including the concentrated acidic media (oleum and trifluoroacetic acid) and high pressures (20-70 bar), as well as the difficulties in product and catalyst recovery. Comparatively, the heterogeneous system becomes more amenable for industrial applications in view of the mild reaction conditions and ease of handling. In this regard, a number of well-known direct alkane upgrading routes based on heterogeneous catalysis such as partial and selective oxidation, oxidative coupling, oxidative dehydrogenation, as well as dehydroaromatization, have been extensively exploited recently, achieving significant improvements in the production of target product.

It is worth to note that these valorization routes are still noncommercialized under lab-scale catalysis testing, because they are facing the dilemmas of: (a) low yield of products. The intrinsic inertly of C–H bond within alkane renders its activation extremely unfavorable even though under the promotion of catalysts, resulting in much lower yield of target product in most cases. (b) Products over-oxidation. The desirable products including methanol, olefin, and ester, are more easily oxidized than alkane, giving rise to the rapid conversion into deep oxidation products, principally CO$_2$. Hence, the selectivity and yield of target products are further limited by the susceptibility of light alkane over-oxidation. (c) Catalyst deactivation. Because the oxidative reactions of alkane are usually highly exothermic, the increase of local temperature within the catalyst bed could almost reach 100°C to 300°C, giving rise to the severely coking and sintering of catalyst. As a result, the metal catalysts have to be regenerated after a short period of operation. (d) Safety problems. The co-feed of alkane and oxygen could form explosive reactive mixture. Giving these problems, the explorations of novel C–H bond activation catalysts as well as advanced reaction processes emerge as the key to convert these light alkanes into target products in a direct and mild manner.

In the review, we intend to provide a comprehensive overview on the important developments of novel heterogeneous catalysts and advanced processes in recent 10 years for the direct conversion of light alkanes, mainly methane, ethane, and propane, into value-added products beyond syngas. This relies on the design and optimization of catalyst materials (single-atom, interfacial site, site confinement and selective blockage), reactants ($\text{H}_2\text{O}_2$, $\text{N}_2\text{O}$, S, and CO$_2$), reaction strategies (chemical looping, $\text{O}_2$ pulsing, tandem reaction), coupled with energy resources (thermocatalysis, electrocatalysis, and photocatalysis). In the end, the technological challenges and our perspectives on the future development in this active research area will be provided.

# 2 | METHANE CONVERSION

Methane is the main component of shale gas, accounting for more than 70% of the total composition, and its conversion into value-add chemicals represents great economic benefits. However, the high stability of C–H bond, negligible electron affinity, and low polarizability within methane render its activation and further conversion into viable and value-added products through less capital-intensive while more selective process being a grand challenge. Apart from the direct combustion, the commercial routes mainly including steam reforming and Andrussow process have the widely recognized limitations by the temperature control and heat management.
as well as generation of toxic intermediates.\textsuperscript{34,58,59} On the other hand, the noncommercial routes for methane conversion could be categorized into oxidative and non-oxidative pathways.\textsuperscript{24} The oxidative pathway, such as partial oxidation of methane (POM) and oxidative coupling of methane (OCM), usually suffers from the poor yield and stability issues, while the nonoxidative pathway, including methane dehydroaromatization (MDA), is strictly hampered by the substantial carbon deposition.\textsuperscript{24,60} Moreover, these thermochemical processes require high temperature, accomplished by the combustion of fossil fuels along with the emission of greenhouse gas CO\textsubscript{2}.\textsuperscript{61} Therefore, innovations in catalysts and processes are highly desirable for the direct conversion of methane.

### 2.1 Partial oxidation of methane

With the ever-increasing demand of methanol and acetic acid as the building blocks for the production of chemicals, the direct conversion of methane into these oxygenated hydrocarbon products becomes more and more appealing. So far, many metal catalysts have been prepared and tested for POM, among which the transition-metal-containing zeolites appears to be the most promising catalyst.\textsuperscript{62} In most cases, the POM imitates by the activation of C–H bond, and its derivated oxygenated products are easily to be over-oxidized due to the favorable thermodynamics.\textsuperscript{24} Hence, in order to preserve these targeted oxygenated products, some novel strategies have been proposed and applied in recent studies.

Flytzani-Stephanopoulos and coworkers have prepared the Rh-based single-atom catalyst (SAC) on the zeolite (ZSM-5) support and tested it for the POM, achieving a production of 0.4 kg of acetic acid per kilogram of catalyst per hour with high acetic acid selectivity of 60% to 100% under the pressure lower than 30 bar (Figure 1A).\textsuperscript{63} It has been suggested that the C–H bond activation could be facilitated by the isolated Ru\textsuperscript{+} cation, giving rise to the formation of RH–CH\textsubscript{3} species. As a result, these species could be functionalized into Rh-OCH\textsubscript{3} and RH–COCH\textsubscript{3} intermediates upon the

![Figure 1](https://example.com/figure1.png)

**Figure 1** A, Mild oxidation of methane to methanol or acetic acid on supported isolated rhodium catalysts. Reproduced with permission: Copyright 2017, Springer Nature.\textsuperscript{63} B, The zeolite model with paired and isolated Al atoms located at the pore mouth of the side pocket. Reproduced with permission: Copyright 2015, Springer Nature.\textsuperscript{66} C, Catalytic cycle for methane oxidation to CH\textsubscript{3}OOH using H\textsubscript{2}O\textsubscript{2} over Fe/ZSM-5. Reproduced with permission: Copyright 2011, Wiley-VCH\textsuperscript{68}
insertions of O and CO, further converting into methanol and acetic acid, respectively. Along this line, Huang and coworkers found that the CeO2 nanowires supported Rh single-atom (SAs Rh-CeO2 NWs) exhibited 6.5 times higher yield of the oxycarbons compared with Rh clusters prepared by wet-impregnation method. It has been suggested that SAs Rh could selectively activate CH4 to *CH3 and gave rise to the formation of oxygenate in the presence of H2O2, while Rh cluster favored the over-oxidation of CH4 to form CO2 with low selectivity and yield of oxygenates. Tao and coworkers reported the transformation of methane into acetic acid and methanol over single-site Rh1O5 within the micropores of ZSM-5. It was found that the anchored Rh3O5 sites demonstrated more than 1000 times higher catalytic activity compared to the free Rh34 cations in the solution without compromising selectivity (~70%) under mild conditions (150°C).

The well-known spatial confinement strategy was also adopted to the POM by Lercher and coworkers based on in situ XAS characterization and DFT calculations. The zeolite mordenite (MOR) with abundant Al in the side pockets was selected to prepare the Cu-MOR materials by copper exchange. The confinement provided by the mordenite micropores was suggested to selectively stabilize the trinuclear Cu-oxo clusters ([Cu3(m-O)3]2−) via anchoring to the two framework Al atoms within the 8-MR side pockets as shown in Figure 1B. As a result, the concentrated and uniform distribution of these isolated active sites provided much higher reactivity for the activation of C−H bond and the subsequent production of methanol. Moreover, Yoshizawa and coworkers found that the small-pore Cu-exchanged zeolites, including Cu-SSZ-16 (Cu-AFX), CuSSZ-13 (Cu-CHA), and Cu-SSZ-39 (Cu-AEI), exhibited much higher catalytic activity to produce methanol than the medium-pore Cu-ZSM-5 (Cu-MFI) zeolite and large-pore Cu-mordenite (Cu-MOR) zeolites, which could be ascribed to their low activation energies for C−H bond dissociation despite of their similar confinement effects.

In addition to the above strategies, the replacement of aggressive O2 with soft oxidants, such as H2O2 and N2O, could conceivably alleviate the over-oxidation of methane to improve the yield of target product. Hammond et al reported the selective oxidation of methane by the oxidant H2O2 over Fe-ZSM-5 catalyst in aqueous condition. Based on catalytic, spectroscopic, and computational results, the interactions between H2O2 and Fe-ZSM-5 were suggested to give a low-energy pathway for methanol production via the formation of primary intermediate, methyl hydroperoxide (CH3OOH) as demonstrated in Figure 1C. Furthermore, they found that the reaction over Au-Pd catalyst proceeded by a distinct mechanism, in which both methyl (•CH3) and hydroxyl (•OH) radicals were detected by electron paramagnetic resonance spectroscopy. As a result, the reaction between H2O2 with •CH3 gave rise to the formation of CH3OOH and then methanol. Recently, they studied the effects of co-feed of H2O2 and O2 as oxidants on the similar Au-Pd catalyst under moderate reaction conditions of 30 bar and 50°C. The ultrahigh selectivity of methanol of 92% was explained by the formation of •CH3 radicals over •OH-assisted C–H bond activation and subsequent reaction with O2 to produce methanol. Sklenak and coworkers found that the abstraction of O from N2O by two M(II) cations (M=Co(II), Ni(II), and Fe(II)) within cation-exchanged ferrierite gave rise to the formation of active site, α-oxygen, responsible for the selective conversion of methane into methanol, formaldehyde, and formic acid.

### 2.2 Oxidative coupling of methane

The catalytic OCM provides a new strategy to produce C2 hydrocarbons such as ethylene. Typically, OCM undergoes the activation of methane to methyl radicals (•CH3) on the surface of catalyst, usually metal oxides and doped oxides, followed by the radicals desorption and coupling in the gas phase to generate ethane, which can be further oxidative dehydrogenated into ethylene. Similar to POM, the main challenge of OCM still lies on the over-oxidation to give more thermodynamically favorable CO2 with low selectivity and yield of ethylene.

In order to weaken the thermodynamic driving forces for over-oxidation, alternative oxidants could potentially address the above problem by selectively converting methane into target ethylene. Sulfur has been suggested by Marks and coworkers as a promising soft oxidant for the catalytic OCM over MoS2, RuS2, TiS2, PdS, and Pd/ZrO2 catalysts. Through experimental and theoretical investigations, they found that the methane conversion is highly dependent on the strengths of surface metal-sulfur (M=S) bond: the weak M=S bond easily abstracted H from methane and strongly interacted with the resultant methyl radicals (•CH3); while the strong M=S bond gave rise to weak C=S bond, and enhanced C−C coupling for the formation of ethylene. Hence, the weak and strong M=S bonds were mainly responsible for the conversion of methane and selectivity of ethylene, respectively. As a result, the Pd/ZrO2 catalyst was found to undergo the evolution into Pd14S7 with stronger M=S bonding and demonstrate the highest catalytic performance. By further optimizing the operation conditions, for example, high CH4/S ratio, short contact time and the provision of a support, the efficiency of CHx
intermediates coupling was significantly promoted with ethylene selectivity approaching 20%. As a consecutive effort, they further studied the OCM by S$_2$ (SOCM) over 10 oxides. It was found that the Mg, Zr, Sm, W, and La-based oxide catalysts suffered from severe coking and delivered limited ethylene selectivity, while Fe, Ti, and Cr-based oxide catalysts coked to a minor extent and exhibited much higher selectivity. Notably, the highest ethylene selectivity of 33% was achieved by further optimizing the reaction conditions, which was comparable to that of noble metal catalysts.

Moreover, Nguyen et al developed a high-throughput screening instrument enabling an automatic performance evaluation of 20 catalysts in 216 reaction conditions for this reaction, which afforded a dataset comprised of 12 708 data points for 59 catalysts in three successive operations. It was demonstrated that the trade-off between the CH$_4$ conversion and C$_2$ selectivity restricts the yield of C$_2$ product, while Mn$-$Na$-$W$-$Si has been suggested to give the best C$_2$ yield. Recently, Lu and coworkers prepared the TiO$_2$-doped Mn$_2$O$_3$-Na$_2$WO$_4$/SiO$_2$ catalyst and achieved 26% methane conversion and 76% C$_2$-C$_3$ selectivity. After careful characterization, they attributed the high catalytic performance to the low-temperature Mn$^2+$$\rightarrow$Mn$^3+$ cycle for O$_2$ activation by MnTiO$_3$, which could work with Na$_2$WO$_4$ synergistically to selectively convert methane to C$_2$-C$_3$ products.

### 2.3 Methane dehydroaromatization

Compared to the above two oxidative pathways, the non-oxidative MDA into aromatics, such as benzene, naphthalene, and toluene, over zeolite supported metal catalysts could effectively avoid the problem of over-oxidation and provide a high selectivity of target product. However, due to the absence of oxygen, the practical application of MDA is still limited by the unfavorable thermodynamics, and the reasonable methane conversion is generally achieved above 700$^\circ$C, causing the stability issue of short lifetime by severe coke formation. Therefore, the design and preparation of efficient catalyst for C$-$H bond activation while minimizing the formation of unwanted graphitic/polyaromatic coke appear to be the core for the commercialization of MDA.

Hensen and coworkers demonstrated a strategy of periodically pulsing O$_2$ into the methane feed as schematically shown in Figure 2A for the substantial stabilization of MDA over the Mo/HZSM-5 catalyst. The employment of $^{13}$C isotope labeling of methane revealed that the oxygen mainly reacted with Mo$_6$C to generate MoO (Figure 2B), which could further catalyze coke oxidation for its removal. The O$_2$ pulsing frequency was further optimized to meet the coke formation rate as shown in Figure 2C-2F, resulting in two times higher benzene yield with respect to the reference by a methane-only feed. Recently, they have shown that the catalytic activity of Mo/HZSM-5 could be significantly enhanced by almost an order of magnitude via raising the reaction pressure to 15 bar.

Xu and coworkers developed a strategy of coupling MDA with chemical looping to achieve reactive separation of H$_2$, which involved a four-step cycle, that is, dehydroaromatization on the Mo/H-ZSM-5 catalyst, hydrogen removal, regeneration on the Fe$_2$O$_3$/FeO redox pair, and water removal on Zeolite 5A. Due to the removal of H$_2$ for improving the equilibrium methane conversion, it rendered a possible aromatics yield up to >40% for this proposed process. Similarly, Caro and coworkers performed this reaction in a hydrogen-permeable ceramic hollow fiber membrane reactor of the composition La$_{5.5}$WO$_{6.6}$Fe$_{8.4}$O$_{11.25}$-$\delta$ (LWM0.4) for the in situ removal of H$_2$ to overcome the thermodynamic constraints. As a result, the yield of aromatics could be increased by ~50% to 70% with respect to the fixed-bed reactor, and the catalyst could be completely regenerated after combustion of the coke with air.

Gascon and coworkers further studied the origin of the high catalytic performance of Mo by a comparison with HZSM-5 zeolite supported Fe catalyst. The surface abundance of mono- and dimeric Mo species, coupled with their favorable carburization to carbide species as active phase, as well as their strong capabilities for C$-$H bond activation contributed to the ultrahigh catalytic activity. Apart from Mo-based catalyst, Li et al performed the thermal nonoxidative aromatization by GaN catalysts. It was revealed that the commercial GaN powders could efficiently transform light alkane into benzene with high activity and selectivity.

### 2.4 Methane conversion to olefins, aromatics, and hydrogen

Based on the above discussion, it can be seen that the over-oxidation of methane and severe coke formation are the main disadvantages for OCM and MDA, respectively. As an alternative pathway, the methane conversion to olefins, aromatics, and hydrogen has aroused a worldwide interest since it was first reported in 2004 by Bao and coworkers, because it combines the merits of OCM and MDA and circumvents their disadvantages. They developed a novel catalyst of lattice-confined single Fe sites embedded in a silica matrix (Figure 3A-C), which catalyzed the efficient generation of methyl radicals (•CH$_3$) without oxidants for further over-oxidation to
**FIGURE 2**  A, Strategy and experimental setup for O₂ pulses to methane dehydroaromatization. B, $^{12}$CO and $^{13}$CO formation upon O₂ pulsing and switching from $^{12}$CH₄ to $^{13}$CH₄ for the Mo/HZSM-5 catalyst at 700°C. Benzene yield as a function of time on stream at O₂-pulsing frequencies of, C, 2 mL/12 minutes, D, 2 mL/6 minutes, E, 2 mL/3 minutes, and, F, 2 mL/2 minutes. Reproduced with permission: Copyright 2016, Wiley-VCH.

**FIGURE 3**  A, STEM-HAADF image and the computational model. B, In situ XANES upon activation, and, C, Fourier transformed (FT) $k^3$-weighted $\chi(k)$-function of the EXAFS spectra of Fe/SiO₂ catalyst. D, DFT calculations on catalytic generation of methyl radicals. E, Long-term stability test of 0.5% Fe©SiO₂ under 1293 K and 14.5 L·g<sub>cat</sub>⁻¹·h⁻¹. Reproduced with permission: Copyright 2016, Science Publishing Group.
CO$_2$ (Figure 3D). After desorption from the catalyst surface, these radicals underwent multiple gas phase reactions (coupling, dehydrogenation, and cyclization) at high temperature to produce ethylene, benzene, and naphthalene. It was stressed that due to the absence of proximity, these spatial-isolated Fe sites could preclude surface C–C coupling for the coke formation over catalyst surface. As a result, it provides a much higher methane conversion of 32%, ethylene selectivity of 52.7% with the total hydrocarbon selectivity exceeding 99%, running for 60 hours without deactivation as shown in Figure 3E.

Recently, Kim and coworkers prepared the Fe©CRS catalyst by the melt-fusing method of fayalite and quartz, which exhibited a higher resistance to structural sintering and coke deposition during this process.\(^8^3\) It was demonstrated that the partially reduced Fe$_3$O$_4$ were transformed into carbides in the melt-fused catalysts, in which the confined Fe were more favorable for the formation of methyl radical and resistant to coke formation compared with Fe$_3$C clusters, achieving 86.2% C$_2$ selectivity at 6.9% to 5.8% methane conversion at 1080°C for 100 hours.

### 2.5 Photocatalytic methane conversion

Compared with the above thermal catalytic methane conversion, photocatalysis emerges as a promising technology to activate the strong C–H bond within methane under mild conditions, giving rise to the production of methanol, ethanol, ethane, ethylene, and benzene.\(^4^1\) As a result, the main drawbacks of thermal catalytic methane conversion, including over-oxidation and coke deposition, could be reasonably alleviated. However, there are still limited studies on the photocatalysis for methane transformation with satisfactory selectivity and yield of targeted product.

Yi and coworkers prepared nanosized zinc oxide for methane oxidation under sunlight illumination.\(^8^4\) The photo-generated hole could effectively activate lattice oxygen as the main active site for the abstraction of hydrogen in methane. Further decoration of nano silver served as an electron sink to reduce the recombination of electrons and holes over ZnO surface, and also as a photo-sensitizer to extend the visible light utilization (Figure 4A), thus yielding higher photocatalytic activity. Tang and coworkers provided a strategy of selectively transforming methane into methanol under moderate light irradiation by the atomic dispersion of iron oxide species on TiO$_2$.\(^8^5\) The presence of FeOOH and Fe$_2$O$_3$ could facilitate the separation of electron-hole, lower the reduction potential of H$_2$O$_2$, and avoid oxygen reduction to O$_2^-$, providing four times higher methanol production compared with bare TiO$_2$ as well as more than 97% selectivity. Wang and coworkers introduced Cu species embedded into polymeric carbon nitride (PCN), and for the first time achieved a photocatalytic anaerobic methane conversion with an ethanol productivity of 106 μmol·g$_{\text{cat}}$·h$^{-1}$.\(^8^6\) As depicted in Figure 4B, the incorporation of Cu into PCN could not only govern the generation of H$_2$O$_2$ and its decomposition to •OH, but also create active sites for the adsorption and activation of methane.

Khodakov and coworkers demonstrated a chemical looping strategy based on silver-heteropolyacid-titania catalyst for selectively converting methane into ethane as shown in Figure 4C.\(^8^7\) This process mainly involved the production of methyl radicals by highly dispersed cat-ionic silver under illumination, and the subsequent recombination to almost stoichiometric formation of ethane. The simultaneous reduction to metallic silver could be reversibly regenerated to cationic silver in air under illumination at ambient temperature. As a result, both high methane coupling selectivity of more than 90% and ethane yield of more than 9% were achieved by this photochemical looping process. Recently, a first example of continuous photocatalytic OCM process at ambient conditions was reported by Tang and coworkers, in which the highest C$_2$ product yield of 6.8 μmol·h$^{-1}$ among photocatalytic methane conversion was provided.\(^8^8\) Moreover, the C$_2$ product selectivity could reach 60% comparable to that by conventional thermal catalysis.

### 2.6 Electrocatalytic methane conversion

In addition to thermocatalysis and photocatalysis, the electrocatalysis provides a new route for methane conversion by external electric potentials, in which the activity and selectivity of target product could be tuned by adjusting the electrode potentials. Owing to the change in the driving force, it could break the thermodynamic equilibrium limitation and render the uphill reactions for the production of some useful chemicals, which are unstable under high temperature. Xie and coworkers designed and prepared the redox-reversible layered perovskite Sr$_2$Fe$_{1.5}$Mo$_{0.5}$O$_6$–δ (SFMO) anode for the electrocatalytic oxidation of methane to ethylene.\(^8^9\) It was demonstrated that the metal-oxide interfaces gave rise to strong interactions in the porous electrode scaffolds, not only promoting the activation of methane but also resisting coke formation to enhance the thermal stability. All these factors contributed to the highest C$_2$ product yield of 16.7% (11.5% C$_2$H$_4$ + 5.2% C$_3$H$_6$) with 82.2% selectivity and exceptionally high durability of more than 100 hours under high temperature.
Ma et al designed and prepared the ZrO$_2$/Co$_3$O$_4$ nanocomposite for the selective oxidation of CH$_4$ to 1-propanol and 2-propanol under an electrochemical method. The acetaldehyde was identified as the key intermediate for the production of 1-propanol with the participation of CH$_4$ by a free radical addition reaction with Co$_3$O$_4$ and carbonate as the catalyst and electrolyte, respectively, giving an efficiency of more than 60% for the production of long-term stable products.

3 | ETHANE CONVERSION

Ethane is the second abundant component of shale gas and also an important accompanying gas of waste effluent in petrochemical industry, motivating us to develop highly efficient ethane activation techniques. The activation of ethane is still facing the challenge of much higher energy consumption for breaking the C–H bond within ethane than that in ethylene and ethyne, and almost all the ethane conversion processes possess positive $\Delta G_0^\circ$, except for the direct ethane combustion with oxygen. As a result, there is an urgent demand for the value-added and energy-saving pathways with efficient catalysts for ethane conversion.

3.1 | Partial oxidation of ethane

Inspired by the POM, the partial oxidation of ethane (POE) to useful oxygenates, including ethanol, acetic acid, and acetaldehyde, appears to be a very attractive
route to produce chemical commodities. However, compared with POM, only a limited study has been conducted in this area using heterogeneous catalysts at low temperature.

Hutchings and coworkers found that Fe- and Cu-incorporated ZSM-5 catalysts were highly active for POE with H$_2$O$_2$ to produce oxygenates with the selectivity of 95.2% and yield of 65 mol-kg$_{cat}^{-1}$-h$^{-1}$.$^{93}$ Moreover, the ethane conversion and acetic acid selectivity could reach about 56% and 70%, respectively. A detailed analysis suggested that ethane underwent a complex reaction network compared with POM using the similar catalyst, in which the oxidation of ethane produced a series of C$_2$ product followed by C$\cdots$C bond cleavage to C$_1$ product. As a result, the key to obtain higher C$_2$ product yield relied on stabilizing the C$_2$ product over catalyst surface to resist the C$\cdots$C bond cleavage by further catalyst design and optimization. As a consecutive effort, they conducted this reaction by utilizing a trickle bed reactor, which could effectively suppress C$\cdots$C bond cleavage and over-oxidation to CO$_2$.\cite{94} The influences of reaction temperature, pressure, reactant concentration together with catalyst composition were further investigated, and a single pass conversion of ethane (22%) to acetic acid (73%, 16% yield) was achieved under the optimized reaction conditions.

Ma and coworkers used nanodiamond (ND) as the catalyst support to immobilize iridium cluster (Ir$_n$/ND) and atomically dispersed Ir (Ir$_1$/ND) catalysts, and compared their catalytic activities for the POE to produce oxygenates.\cite{95} It was found that Ir$_n$/ND displayed much higher catalytic activity and stability for the production of C$_2$ oxygenates in the aqueous phase by O$_2$ and CO, ascribed to its slightly oxidized Ir species in low-valence state stabilized by CO. Moreover, Tao and coworkers confined the single-atom sites Rh$_{12}$O$_3$ within the micropores of H-ZSM-5, which could highly promote the oxidation of ethane by hydrogen peroxide to produce acetic acid and formic acid.\cite{96}

### 3.2 Oxidative dehydrogenation of ethane

Ethylene remains the largest petrochemical commodity produced around the world, whose production, mainly involves naphtha and gas oil steam cracking, also ranks the second largest contributor of energy consumption. In addition, the ethane steam cracking by co-feeding ethane and steam into high-temperature reactor tubes for gas-phase cracking has also demonstrated some advantages for ethylene production.\cite{97} Notably, the limited equilibrium conversion, over-oxidation to produce CO$_2$, severe coke deposition, and intensive energy demand are still the main problems for its industrial application. As an alternative route, the oxidative dehydrogenation of ethane (ODH) has gained worldwide attention from chemists, which uses oxygen to combust the abstracted hydrogen and makes the overall reaction exothermic to remove the equilibrium constraint.\cite{37} Despite these advantages, the development of highly efficient catalyst and the elimination of safety hazards by co-feeding ethane and oxygen emerge as the ultimate challenges for this process.

Lercher and coworkers reported the ODH of ethane over the catalysts involving a mixed molten alkali chloride covered Dy$_2$O$_3$-doped MgO, LiKCl/MgO + Dy$_2$O$_3$.\cite{98} It was identified the oxyanionic OCl$^{-}$ as the main active species, provided by Cl$^{-}$ oxidation on MgO surface. To accomplish the catalytic cycle, O$_2$ was further dissolved into the alkali chloride melt and dissociated into oxygen to replenish the oxygen vacancies on MgO. The reaction was suggested to proceed by a Mars-van-Krevelen-mechanism via two coupled steps at the solid-liquid and gas-liquid interface (Figure 5A), this oxynion reductively dehydrogenates ethane with nearly ideal selectivity up to 95%. Similarly, Li and coworkers also prepared the molten Li$_2$CO$_3$-modified La$_{0.8}$Sr$_{0.2}$FeO$_3$ (LSF) catalyst, and demonstrated a strategy of chemical looping for the oxidative dehydrogenation (CL-ODH) of ethane, which gave rise to the redox catalyst of LSF substrate covered by a molten Li$_2$CO$_3$ layer during working state.\cite{99, 100} It was found that the reduction of Fe$^{4+}$ to Fe$^{3+}$ facilitated the formation of active peroxide species (O$_2^{2-}$) over LSF surface, followed by transferred from the inner to outer surface of Li$_2$CO$_3$ layer for the ODH reaction as shown in Figure 5B. Hence, the molten layer could not only help transfer active peroxide species but also block the non-selective sites, achieving >90% ethylene selectivity and 59% ethylene yield. Similarly, the Na$_2$WO$_4$-promoted Mg$_3$MnO$_8$-based redox catalysts have been also developed by them for this reaction proceeding by parallel gas-phase cracking of ethane and selective combustion of H$_2$.\cite{101, 102}

Recently, a highly efficient M1 type crystals MoVTeNbO$_x$ catalyst was prepared under hydrothermal conditions.\cite{103} As shown in Figure 5C, the formation of M1 crystals with highly corrugated side walls was suggested to provide a high concentration of active sites, accounting for the high activity. Yi and coworkers further incorporated Ce into this MoVTeNbO catalyst, which achieved 56.2% of ethane conversion and 95.4% of ethylene selectivity after 200 hours catalytic testing.\cite{104} In addition, Wang and coworkers proposed the uses of S-modified NiAl mixed-oxide and N$_2$O as the catalyst and oxidant, respectively, for ODH to ethylene.\cite{105} It was found that S could alter the chemical state of Ni and isolate electrophilic oxygen (O$^-$) species, which were...
favorable for the proper cleavage of the C–H bond of ethane to produce ethylene instead of CO2 (Figure 5D). As a result, the modified NiAl mixed oxide catalyst achieved a very high ethylene selectivity of ~100% over a wide ethane conversion.

Yue and coworkers demonstrated a photocatalytic process for ODH with CO2 to produce ethylene and syngas over Pd/TiO2 catalysts.106 It was found that the intermediate energy level (provided by the 3d orbital of Pd) and the electron channel (formed via the Pd–O covalent bonding) facilitated the electron transfer, excitation, and separation, where the photo-induced e−, h+, and hydroxyl radical strongly affected this reaction. As a result, the Pd/TiO2 catalyst with 1 wt% Pd loading exhibited the C2H4 and syngas production rates of 230.5 and 282.6 μmol·gcat−1·h−1, respectively. On the other hand, Wang and coworkers demonstrated an electrocatalytic process for ODE.107 It was suggested that the Al2O3/LSCF interfaces could efficiently remove the adsorbed oxygen species, giving rise to significantly enhanced selectivity and stability. Moreover, the electronic structure of interfacial Fe center could be tailored by the formation of Al-O-Fe with increased density of state around Fermi level, which promoted the adsorption and activation of ethane.

3.3 | Direct ethane dehydrogenation

With respect to ODH, the direct dehydrogenation of ethane through a nonoxidative route demonstrates significant advantages in suppressing the over-oxidation of ethylene. The current challenge for the non-ODH relies on the limited lifetime of catalyst by coke deposition, and
activity loss by the reduction of active oxide species to lower valence under the nonoxidative conditions. Hence, the regeneration of catalyst needs to shut down the reactor system to burn the catalyst, and even leach the catalyst to reload the metal, which are time and effort consuming, and particularly expensive for the precious metals.

Xiao and coworkers successfully incorporated the isolated Fe$^{6+}$ sites into the siliceous MFI zeolite framework by the employment of ethylenediaminetetraacetic sodium. Owing to the unique structure (Fe$^{6+}$-1-EDTA), these active Fe$^{6+}$ species could be maintained in resistance of reduction and carbonization, which facilitated the desorption and transfer of ethylene and hydrogen within the zeolites micropores. As a result, it gave extremely high activity (26.3% ethane conversion) and selectivity (97.5% ethylene selectivity) without any deactivation for 200 hours. Shimizu and coworkers treated the In-exchanged CHA zeolite (In-CHA) at high temperatures (>773 K) under H$_2$ atmosphere to prepare the indium hydride species, [InH$_2$]$^+$, which exhibited much higher activity (27.1% ethane conversion) and selectivity (96.9% ethylene selectivity) for the direct dehydrogenation of ethane for more than 90 hours. McIntosh and Shin found that the proton-conducting oxides, including BaZrO$_3$ (BZ) and BaCeO$_3$ (BC) supported Cr catalyst exhibited more than one order of magnitude higher catalytic activity for this reaction compared with $\gamma$-Al$_2$O$_3$ supported one. Further XPS characterization result suggested that Cr$^{3+}$ as the main active oxidation state for ethylene dehydrogenation, which was more prevalent on a barium zirconate support in comparison to barium cerate.

Apart from the metal oxides, the noble metals have been also studied for this reaction. For example, Miller and coworkers found that the addition of Zn into Pt gave rise to the formation of high symmetry Pt$_{1-}$Zn$_{1}$ nanoparticles alloys with isolated Pt surface sites, which exhibited a sixfold higher turnover rate compared to monometallic Pt/SiO$_2$ catalyst. The promotional effect of Zn has been suggested to suppress the hydrogenolysis and cracking of ethane and weaken the bond formation between the Pt 5d orbitals and adsorbates. Li and coworkers prepared supported Pt-In and Pt-Ga nanoparticles with controlled bimetallic composition by colloidal method. It was found that the promoter-rich PtIn$_2$ showed the highest TOF, ascribed to both the strong electronic perturbation to Pt sites and geometric change by the formation of the CaF$_2$ crystal structure. Moreover, He and coworkers reported for the first time a novel electrocatalytic conversion of ethane to ethylene and hydrogen using a proton conducting electrochemical deprotonation cell, achieving almost 100% ethylene selectivity. Notably, the electrocatalytic process could save 65% energy and reduce the carbon emitting by 72% with respect to the traditionally industrial ethane steam cracker. Xie and coworkers reported the electrochemical non-ODH in the anode together with CO$_2$ reduction in the cathode, which exhibited the enhanced ethane conversion of 75.2% with ~100% ethylene selectivity. It was demonstrated that the electrochemical pumping of H$^+$ at metal-oxide interfaces facilitated anode activity, and the interface compositions could further tailor the ethane conversion.

Luo and coworkers demonstrated the preparation of double-layered perovskite (Pr$_{0.6}$Sr$_{0.4}$)$_{3}$(Fe$_{0.85}$Mo$_{0.15}$)$_{2}$O$_7$ (DLP-PSFM) with uniformly dispersed in situ exsolution of Co-Fe alloy nanoparticles, achieving 41.5% of ethylene yield at 750°C, with 91% of selectivity and no CO$_2$ emission.

### 3.4 CO$_2$-assisted dehydrogenation of ethane

The CO$_2$-assisted dehydrogenation of ethane to ethylene, that is, C$_2$H$_6$ + CO$_2$ → C$_2$H$_4$ + CO + H$_2$O, provides an unprecedented opportunity to transform underutilized ethane and greenhouse gas CO$_2$ into value-added chemicals, thus demonstrating great developmental potential and wide industrial application prospect. The competition between two main reaction pathways based on the cleavages of C=C and C–H bonds is suggested to determine the selectivity: (a) the cleavage of C=C bond to produce syngas, C$_2$H$_6$ + 2CO$_2$ → 4CO + 3H$_2$ and (b) the cleavage of C–H bond to produce ethylene, C$_2$H$_6$ + CO$_2$ → C$_2$H$_4$ + CO + H$_2$O. Notably, because the C–H bond (415 kJ·mol$^{-1}$) is thermodynamically more stable than the C=C bond (368 kJ·mol$^{-1}$) within ethane, one of most important issues in the area is selectively converting ethane into more valuable ethylene by breaking the C–H bond while retaining C=C bond. Typically, this process involves the reduction of CO$_2$ to CO in tandem with ethane dehydrogenation to ethylene. In this regard, the design and manipulation of bifunctional catalysts to split the two very different reactants in terms of their activations emerge as the core for this process development.

Chen and coworkers reported a switch between these two pathways by tailoring the interfacial sites of Ni-Fe/CeO$_2$ catalyst: Ni-CeO$_x$ broke both the C=C and C–H bonds to produce syngas, while Fe-CeO$_x$ selectively broke the C–H bond to produce ethylene. Hence, controllable preparation of these two kinds of active sites enabled a rational enhancement in ethylene selectivity. More recently, they found that the ethylene selectivity could be also tuned by oxygen species: the electrophilic (eg, O$^-$, O$_2^-$, O$_2^{2-}$) favor to attack the electron-rich C=C


bond, while nucleophilic (e.g., lattice oxygen) favor to attack the electron-deficient C–H bond. Based on this, the active and nonselective oxygen species on Pd/CeO₂ catalyst facilitated the production of syngas, while the FeOₓ/Pd interface by introducing Fe could selectively break the C–H bond to produce ethylene as shown in Figure 6.

Interestingly, a tandem reactor incorporating the dehydrogenation of ethane to ethylene and the hydroformylation of ethylene to propanal was well designed. Specifically, the first reactor used a FeₓNi₁/CeO₂ catalyst to catalyze CO₂-assisted dehydrogenation of ethane to ethylene, as well as its reforming to produce syngas under 600°C to 800°C, while the second reactor used a RhCoₓ/MCM-41 catalyst to catalyze hydroformylation of ethylene to C₃ oxygenates, including propanal and 1-propanol, under 200°C and ambient pressure. This strategy by coupling two processes provides a promising opportunity to transform ethylene and CO₂ into aldehydes and alcohols. Furthermore, they reported a one-step process for the production of aromatics through the tandem reactions of CO₂-assisted ODH and subsequent aromatization using P and Ga-modified ZSM-5 catalyst at 873 K and ambient pressure, which demonstrated great activity, hydrothermal stability and coke resistance.

4 | PROPANE CONVERSION

In addition to methane and ethane, propane ranks the third component in shale gas, offering the potential feedstock to manufacture hydrocarbons. On the other hand, propylene emerges as a key commodity chemical, ranking as the second place in the most-produced petrochemical feedstock in the United States. Typically, the thermal cracking and fluid catalytic cracking of naphtha are the two main routes for propylene production in industrial, which usually suffer from severe coke deposition and low propylene yield. Hence, the development of efficient catalysts and processes to convert the abundant propane into propylene via direct or indirect dehydrogenation is highly desirable for propane utilization.

FIGURE 6 The strategy to tune the selectivity of syngas and ethylene from CO₂-oxidative dehydrogenation of ethane (ODH) of ethane based on the interfacial interactions. Reproduced with permission: Copyright 2020, Cell Publishing Group
4.1 | Direct propane dehydrogenation

The direct dehydrogenation of propane to propylene is the most direct route to produce propylene. However, the inherent reaction characters pose some technical limitations and constraints for its real application: the high endothermic nature with increased molecular number requires the reaction operated under high temperature and low partial pressure than 1 atm to achieve reasonable propylene yield.\(^{124}\)

Lercher and coworkers prepared the Ga/H-ZSM-5 catalyst and identified the Brønsted and Lewis acidic Ga\(^+\) sites as the active site for this reaction.\(^{125}\) Weckhuysen and coworkers developed a novel catalyst consisting of 1000 ppm Pt, 3 wt% Ga, and 0.25 wt % K supported on alumina for this reaction, which was highly active and resistant to coke deposition for a long reaction time. A bifunctional active phase, involving coordinately unsaturated Ga\(^{3+}\) species and Pt as the active species and promoter, respectively, was proposed for this significant improvement.\(^{126}\) Coperet and coworkers demonstrated a strategy to prepare the partially dehydroxylated silica supported Pt-Ga catalyst, which exhibited much higher activity, selectivity, and stability for direct dehydrogenation of propane.\(^{127}\) The sequential grafting of a Pt precursor onto silica with isolated gallium sites followed by H\(_2\) reduction gave rise to the formation of a Ga\(_x\)Pt (0.5 < x < 0.9) alloy with a fraction of isolated Ga sites. As a result, the alloy structure and a support with dispersed Lewis acidic gallium single-sites combined with low Bronsted acidity were suggested to contribute to the high catalytic performance.

Recently, the subsurface of Pt\(_2\)Mn intermetallic subsurface instead of monometallic Pt was found to significantly lower the heats of hydrocarbon and hydrogen adsorption of the surface Pt sites, thus delivering much higher propylene selectivity.\(^{128}\) The relationship between propane dehydrogenation activity and Pt d-band center shift modified by different 3d transition metal atoms in subsurface regions was further established, which could guide the design of efficient catalysts for this reaction.\(^{129}\) The single atom alloys (SAAs) catalysts also demonstrate significant advantages for this reaction. For instance, the γ-alumina-supported platinum/copper (Pt/Cu SAA) catalysts was prepared by Gong and coworkers using an incipient wetness co-impregnation method, which could promote the desorption of propylene in resist to its further dehydrogenation. As a result, it demonstrated much higher propylene selectivity (~90%) and excellent stability (>120 hours) under atmospheric pressure at 520°C.\(^{130}\) Furukawa and coworkers designed and prepared the single-atom Pt in intermetallics catalyst (PtGa-Pb/SiO\(_2\)) by selectively blocking threefold hollow Pt\(_3\) ensembles while maintaining the single-atom-like isolated Pt\(_1\) sites, achieving a high selectivity of 99.6% for propylene production.\(^{131}\) Weckhuysen and coworkers explored the Sn-doped CeO\(_2\) supported Pt single atom catalysts for this reaction.\(^{132}\) The formation of Pt-Sn clusters under reaction conditions were found to be very stable, even during extended reaction at 680°C, enabling the achievement of high selectivity toward propylene production.

In a recent study, Yu and coworkers demonstrated a ligand-protected strategy of encapsulation of sub-nanometer bimetallic Pt-Zn clusters within S-1 zeolite, which gave an ultrahigh propylene selectivity of 99.3% and specific activity of propylene formation of 65.5 mol-C\(_3\)H\(_6\)/mol-Pt h\(^{-1}\).\(^{133}\) Moreover, this PtZn4@S-1-H catalyst exhibited negligible activity loss for more than 216 hours on stream. Using the similar strategy, Liu and coworkers encapsulated the bimetallic Pt-Sn clusters within ZSM-5 (MFI) zeolite by an ultra-fast and in-situ encapsulation method within just 5 minutes, which also gave much higher selectivity.\(^{134}\)

Apart from the noble metals, Kondratenko and coworkers found the coordinately unsaturated Zr cations working as the active site for the dehydrogenation of propane, whose concentration could be further tailored by changing Zr promoter and incorporating a small amount of hydrogenation-active metal.\(^{135}\), \(^{136}\) As a result, the Cu/ZrO\(_2\)-La\(_2\)O\(_3\) catalyst with Cu loading of 0.5 wt% exhibited industrially comparable activity and durability. Gong and coworkers found that the VO\(_x\) supported on ZrO\(_2\) exhibited six times higher catalytic activity than it supported on commercial γ-Al\(_2\)O\(_3\), ascribed to the interaction between VO\(_x\) and ZrO\(_2\) for the formation of low coordinated V species with low C–H bond activation barrier.\(^{137}\), \(^{138}\) Laursen and coworkers reported the high propylene selectivity (~94%), activity (TOF = 4.7 × 10\(^{-7}\) seconds\(^{-1}\)), as well as stability (~94% for the 82 hours) for the direct propylene dehydrogenation over the Ni\(_3\)Ga/Al\(_2\)O\(_3\) catalyst.\(^{139}\) Furthermore, a comparison of the well-defined Si-supported Ni\(_3\)Ga and NiGa catalysts as well as Ni\(_3\)Ga/Al\(_2\)O\(_3\) suggested an optimal catalyst composition between 3:1 and 1:1 Ni:Ga, where Ni as the active site for dehydrogenation and the improved conversion, and Ga for the enhanced selectivity and stability.

4.2 | Oxidative dehydrogenation of propane

Similar to ethane, the oxidative dehydrogenation of propane (ODHP) is regarded as one of the most promising method to produce propylene due to the following reasons: (a) the exothermic nature makes it
thermodynamically unrestricted and (b) the low operation temperature minimizes coke deposition for a long-term stability.\textsuperscript{140} The main challenge for this process relies on the over-oxidation of propane to more thermodynamically favorable CO\textsubscript{2}, thus resulting in much lower propylene yield.

Corma and coworkers studied the confinement of Sn-decorated Pt clusters within the channels of purely siliceous MFI zeolite for the ODHP.\textsuperscript{141} It was suggested that the formation of subnanometric PtSn clusters (0.5-0.6 nm) in terms of their interaction by selective location in the sinusoidal 10R channels of MFI zeolite as shown in Figure 7A was the key to achieve propane conversion of \( \sim 20\% \) and propylene selectivity of \( >97\% \), which had negligible decreases after 70 hours stability test. Hermans and coworkers found that hexagonal boron nitride and boron nitride nanotubes also exhibited high catalytic performances of 14\% propane conversion, 79\% propene and 12\% ethylene selectivity, in which the O-terminated armchair boron nitride edges were suggested as the main catalytic active sites.\textsuperscript{142} Peng and coworkers demonstrated that the incorporation of N into CNT could promote the ODHP, ascribed to the significantly lower energy for oxygen activation.\textsuperscript{143}

Farha and coworkers reported the preparation of Zr-based metal-organic framework (MOF) NU-1000 supported cobalt-oxide clusters as an active, selective and stable catalyst for the ODHP (Figure 7B).\textsuperscript{144, 145} A series

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**FIGURE 7**  
A, Structural evolution of K-PtSn@MFI during reduction with H\textsubscript{2}. Reproduced with permission: Copyright 2020, Springer Nature.\textsuperscript{141} B, Structural representation of the metal-organic framework (MOF) support, NU-1000, as well as the two preparation methods of Co-based catalysts for propane oxidative dehydrogenation of ethane (ODH) catalysis. Reproduced with permission: Copyright 2017, American Chemical Society\textsuperscript{145}
of promoter ions including Ni(II), Zn(II), Al(III), Ti(IV) and Mo(VI), were selected to decorate the NU-1000 followed by Co(II) ion deposition to prepare the bimetallic-oxo, hydroxo, aqua clusters. It was found that the catalytic activity increased with the decreased Lewis acidity of the promoter ion, following the order of Mo(VI) < Ti(IV) < Al(III) < Zn(II) < Ni(II). In addition to O₂, CO₂ was also employed as a soft oxidant for the dehydrogenation of propane. Demonstrated by Chen and coworkers, both the bulk Fe₃Ni (111) surface and the FeO/Ni (111) interface were found to facilitate the cleavage of C—H bond to produce propylene, while the Pt-terminated Ni₃Pt (111) promoted the cleavage of C—C bond to produce syngas.¹⁴⁶ As a result, the Fe₃Ni and Ni₃Pt catalysts were selective for propylene and syngas, respectively. Furthermore, Hutchings and coworkers demonstrated the role of CO₂ in the ODHP over the Pd/CeZrAlOₓ catalyst, which regenerated the selective oxygen species and shifted the equilibrium by consuming H₂ through the reverse water-gas-shift reaction.¹⁴⁷

Furthermore, compared with methane and ethane, the studies on photocatalytic conversion of propane are limited. Song and coworkers reported a novel nonthermal plasma-assisted photocatalytic approach for the conversion of propane into C₂-C₉ branched-chain paraffins, with 48.6% of propane conversion, 58.4 C% of paraffins yield, and limited coke deposition (6.3 C%). The synergy between plasma activation and photocatalysis is believed to open up a new avenue in the upgrading of propane.¹⁴⁸

5 | CONCLUSION AND PERSPECTIVE

This review provides the recent progresses and strategies on the development of heterogeneous catalysts and processes to transform alkane, mainly methane, ethane, and propane, into value-added chemical commodity. In order to selectively convert alkane into target product with long operation period, extensive efforts have been devoted to solving three essential issues, that is, C—H bond activation, product over-oxidation, and coke deposition, which are highly relevant to the activity, selectivity, and stability of catalytic processes, respectively.

First, given the strong energy of C—H bond within alkane, the design and manipulation of novel metal catalyst to facilitate its cleavage are the prerequisites for alkane conversion. In light of the high coordination unsaturation, the single atom and isolated site catalysts could strongly interact with alkane to activate the C—H bond for its conversion. Similarly, the confinement of active site has also demonstrated great potentials for alkane activation considering its significant influences on the geometric and electronic properties of metal site. Moreover, the use of zeolite catalysts with uniform pore structures in shape-selective catalysis is a field undergoing rapid growth in recent years especially in petrochemical process technology. Hence, the combination of the above factors by selectively confining single atom site within the pore-controllable zeolites may give rise to the production of hydrocarbons with a certain chain length.

Second, the shift from thermocatalysis to photocatalysis and electrocatalysis by changing energy resources also endows us with good opportunity to activate alkane for its conversion under ambient conditions, which can significantly lower the consumption of energy as well as operation cost. However, as far as we are concerned, the catalytic performances of photocatalysis and electrocatalysis for alkanes conversion are still far from that of thermocatalysis due to the limited C—H bond activation ability, and the relevant reaction mechanism is still unclear in terms of the complex factors under photocatalysis and electrocatalysis environments. Moreover, the combinations of the above two energy resources are rarely studied. As such, future research could also focus on synergizing the advantages of photocatalysis and electrocatalysis for highly efficient alkane conversion.

Third, considering O₂ is widely employed to promote alkane activation, the over-oxidation of target product toward thermodynamically favorable CO₂ is highly expected to be suppressed. Among a wide range of soft oxidant, CO₂ has emerged as the most promising alternative of O₂ for alkane conversion. On the other hand, CO₂ could deliver monoatomic oxygen species over catalyst surface to activate alkane, instead of strongly oxidized dioxygen species. On the other hand, CO₂ as a greenhouse gas is widely existed in the nature, and its conversion into value-added chemicals is highly economic and environmentally friendly. Notably, CO₂ could also serve as the reactant for alkane dry reforming to produce syngas. Based on these factors, it is reasonable to assume that the combination of CO₂-assisted oxidative dehydrogenation and dry reforming by using bifunctional catalysts possesses the potentials to produce the mixed gas of alkene, CO and H₂, which could further convert into propionaldehyde and butyraldehyde by hydroformylation. Moving forward, the integration of oxidative dehydrogenation, dry reforming and hydroformylation into one system for the in situ production of aldehyde remains highly desirable yet challenging in future study.

Fourth, from the point view of stability, both the design of functionalized catalyst and the development of advanced process could be applied to inhibit coke deposition during reaction. The preparation of isolated catalytic site has witnessed a significant improvement in catalytic
stability due to the suppressed unwanted C—C coupling reactions for coke formation over adjacent catalytic sites. Moreover, periodic supply of short pulses of oxygen into alkane feed over a fixed bed could effectively remove coke over catalyst surface, which provides a unique insight into the role of oxygen during alkane transformation. With the aim to commercial application, the next step could rely on the exploration of suitable reactor configurations to realize these novel catalysts and advanced processes.

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ORCID
Xuezhi Duan https://orcid.org/0000-0002-5843-5950
De Chen https://orcid.org/0000-0002-5609-5825

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AUTHOR BIOGRAPHIES

**Wenyao Chen** received his BS and PhD degrees from East China University of Science and Technology (ECUST) in 2013 and 2018, respectively. After a stay as post-doctoral fellow in the University of Toronto, Canada, he joined the faculty of the State Key Laboratory of Chemical Engineering at ECUST. His current research interests include kinetics-assisted design and manipulation of metal catalysts for energy conversion.

**Xuezhi Duan** received his PhD degree in chemical engineering from East China University of Science and Technology (ECUST) in 2012. After a 2-year (2013-2015) stint with Prof D. C. as a VISTA Scholar at Norwegian University of Science and Technology, he joined the faculty of School of Chemical Engineering at ECUST. He is now a full distinguished professor and deputy director of the State Key Laboratory of Chemical Engineering. His current research interests include kinetics-assisted catalyst design, theoretical calculations, and reactor engineering. In addition, he received the Young Scientist Prize awarded by the International Association of Catalysis Societies, the Outstanding Youth Award of Global Chinese Chemical Engineers Symposium, and so forth.

**Xinggui Zhou** received his BS and PhD degrees from East China University of Science and Technology (ECUST) in 1987 and 1996, respectively. He became an associate professor in 1997 and a full professor in 2002 at ECUST. He was entitled as a Dawn Scholar of Shanghai by the Education Commission of Shanghai in 2001, Elitist of the New Century by the MOE in 2005, and Lading Talent of Shanghai in 2018. He is now the director of the State-Key Laboratory of Chemical Engineering at ECUST and the coordinator of the 111 Project of Reaction Science and Engineering. His current research interests include catalysis and reaction engineering, microreactor technology, and industrial crystallization.

**De Chen** received his PhD degree from the Norwegian University of Science and Technology (NTNU) in 1998. In the same year, he joined the Department of Chemical Engineering of the same university as an associate professor, and in 2001, he became a professor at the same department. His current research interests include heterogeneous catalysis and nanomaterials for new technologies, which incorporates the use of catalysis in the synthesis of nanocarbon materials and their application as catalysts, catalyst supports, and as electrodes in fuel cells, supercapacitors, and batteries, the use of catalysis in natural-gas conversion, hydrogen production, and biomass conversion, and the use of these materials as sorbents for CO2 capture at high temperatures.

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