Abstract CO₂-assisted oxidative dehydrogenation of propane (CO₂-ODHP) is an attractive strategy to offset the demand gap of propylene due to its potentiality of reducing CO₂ emissions, especially under the demands of peaking CO₂ emissions and carbon neutrality. The introduction of CO₂ as a soft oxidant into the reaction not only averts the over-oxidation of products, but also maintains the high oxidation state of the redox-active sites. Furthermore, the presence of CO₂ increases the conversion of propane by coupling the dehydrogenation of propane (DHP) with the reverse water gas reaction (RWGS) and inhibits the coking formation to prolong the lifetime of catalysts via the reverse Boudouard reaction. An effective catalyst should selectively activate the C–H bond but suppress the C–C cleavage. However, to prepare such a catalyst remains challenging. Chromium-based catalysts are always applied in industrial application of DHP; however, their toxic properties are harmful to the environment. In this aspect, exploring environment-friendly and sustainable catalytic systems with Cr-free is an important issue. In this review, we outline the development of the CO₂-ODHP especially in the last ten years, including the structural information, catalytic performances, and mechanisms of chromium-free metal-based catalyst systems, and the role of CO₂ in the reaction. We also present perspectives for future progress in the CO₂-ODHP.

Keywords Propane; Dehydrogenation; Propylene; CO₂; Chromium-free metals; Catalytic performance

1 Introduction

Propylene is a mainstay in the C3 industry, which can be used to prepare basic organic chemicals through a variety of reaction pathways, such as polypropylene (PP) [1], propylene oxide (PO) [2], acrylic acid (AA) [3], acetone [4], acrylonitrile [5], isopropanol [6], and butanol [7] (Fig. 1). The high-abundance downstream products of propylene are widely used in the terminal fields of home appliances, textiles, building materials, automobiles, electronic appliances, and health care, etc., which support the increasing demand for propylene. Especially, the global demand for the medical mask prepared by melt-blown fabric which is a material manufactured from polypropylene had risen sharply even suffered a shortage for the COVID-19 since 2020. Thus, the great demand for PP has further promoted the production of propylene.

The conventional synthetic methods of propylene involve fluid catalytic cracking (FCC) and steam cracking of naphtha, light diesel, and other oil by-products, in which propylene is obtained as one of the co-products [8]. More than 75% of propylene were produced by FCC and steam cracking technologies in 2020 (Fig. 1). However, these methods cannot meet the fast-increasing demand of propylene for the low selectivity to propylene and the rapid consumption of fossil resources [9]. Therefore, to develop...
more efficient technologies for fabricating of propylene such as dehydrogenation of propane (DHP) [10], methanol-to-olefins (MTO) [11], coal-to-olefins (CTO) [12], Fischer–Tropsch to Olefins (FTO) [13], and C4 olefin disproportionation technology [14] is highly important. Among them, the DHP technology, as an on-purpose route to obtain propylene, has gradually become the main force to produce propylene in recent years (Figs. 1 and 2).

Indeed, the DHP technology was greatly promoted in recent years, which is benefited from a blowout of propane yield due to the success of the shale gas revolution in the USA [15–17]. In 2019, shale gas production reached 6321.2 billion cubic meters, accounting for 30% of the total natural gas production in the USA, and the compound annual growth rate of shale gas in the past ten years reached 16.5% (Fig. 3). Propane, relying on shale gas, has also flooded into the global energy market to lower the price of propane and makes the DHP technology profitable. Thus, dehydrogenation technologies including FBD-4, Catofin, Oleflex, PDH, STAR, ADHO, FCDh, and K-PROTM have been widely established, whose catalysts mostly involve Pt-based and CrOx-based materials (Table 1) [9, 18, 19]. Nonetheless, the DHP is a strong endothermic ($\Delta H = +124$ kJ·mol$^{-1}$) and pressurized reaction and is not only limited by thermodynamic equilibrium but also by kinetics. The high-temperature condition is essential for the reaction [20]; however, the cleavage of the C–C bond in hydrocarbons under high-temperature conditions, which impels the occurrence of side reactions such as deep dehydrogenation, oligomerization, and coking, results in a significant decrease in propylene selectivity and formation of coke deposits [21]. Besides, under harsh conditions, the catalysts are liable to sintering and irreversible deactivation [20–22]. In addition, the precious Pt metal and highly toxic Cr catalysts are employed in the DHP reaction, and this increases investment cost and environmental burden, which goes against sustainable development.

Thus, the oxidative dehydrogenation of propane (ODHP) is an attractive route to substitute the DHP route due to its exothermicity, and it can break away from thermodynamic limitation even at low temperatures [23].
Nowadays, the traditional ODHP with O$_2$ as an oxidizing agent (O$_2$-ODHP) has been extensively studied by employing transition metal oxide catalysts with redox characters, such as chromium [24], vanadium [25–27], and molybdenum [28, 29]. In addition, the hexagonal boron nitride (h-BN) has been discovered as a potential catalyst for the O$_2$-ODHP reaction, which exhibited a high catalytic activity (14% conversion of propane and 79% selectivity to propylene at 490°C) and well-suppressed overoxidation [23, 30–32]. However, the inevitable overoxidation of hydrocarbons or propylene to carbon oxides (CO$_x$) is an urgent reason for lowering the selectivity of olefins.
(propylene and ethylene). Along with the exploitation of efficient catalysts for improving the propylene selectivity, the use of a soft oxidant such as CO$_2$ to replace O$_2$ has become another way to solve the problems in the O$_2$-ODHP reaction [33].

On the other hand, after the industrial revolution, the amount of CO$_2$ emissions has increased sharply, which causes serious harm to the environment and the global ecosystem [34]. In this background, many countries have pledged to reduce CO$_2$ emission, and among them, in 2020, China proposed a timetable for the peaking CO$_2$ emissions before 2030 and carbon neutrality before 2060 (Fig. 4). After that, many protocols on reducing CO$_2$ concentration were proposed, especially converting CO$_2$ into valuable chemicals. CO$_2$ is a high oxidation state of carbon with a high enthalpy of formation (~ 394 kJ·mol$^{-1}$) and a low chemical potential molecule. Presently, CO$_2$ can be used as a C1 resource to synthesize many valuable chemicals via different pathways, such as reforming of CO$_2$ with methane to syngas [35], CO$_2$ hydrogenation to methanol, dimethyl ether, and hydrocarbon fuels [36–38], CO$_2$ polymerization to dimethyl carbonate [39–42], CO$_2$ carbonation conversion [43], CO$_2$ oxidative dehydrogenation of propane (CO$_2$-ODHP) [44, 45].

Indeed, the CO$_2$-ODHP is endothermic in nature (Reaction (1), $\Delta H_{298}$ = +164 kJ·mol$^{-1}$) as opposed to the O$_2$-ODHP reaction ($\Delta H_{298}$ = −118 kJ·mol$^{-1}$). However, CO$_2$ can consume the H$_2$ in situ produced in the DHP (Reaction (2)) via the reverse water gas reaction (RWGS, Reaction (3)) further shifts the reaction equilibrium to produce more propylene. In addition, the coke deposition can be removed via the reverse Boudouard reaction (Reaction (4)), and thus, the lifetime of catalyst will be prolonged. Furthermore, for a redox metal catalyst, CO$_2$ can re-oxidize the reduced catalyst to promote its recovery and further achieve the reaction. However, the CO$_2$-ODHP reaction is very complicated and can be proceeded via various pathways, some of which associate with side reactions such as CO$_2$ dry reforming of propane (Reaction (5)) and propane cracking (Reaction (6)). Through thermodynamic calculations, Michorczyk et al. [46] found that the equilibrium yield of propylene could be improved by coupling propane dehydrogenation with RWGS reaction. Subsequently, Liu et al. found that propane conversion and propylene selectivity were immediately enhanced after the introduction of a suitable amount of CO$_2$ but suppressed by adding excessive CO$_2$ due to the competitive adsorption of propane and CO$_2$ on the catalyst surface [47]. Therefore, improving the selectivity of CO$_2$-ODHP by inhibiting the side reactions is crucial to obtaining a high propylene yield. Meanwhile, the desorption of propylene in time not only improves the yield of product but also inhibits the formation of coke deposition.

$$
\text{C}_3\text{H}_8 + \text{CO}_2 \rightarrow \text{C}_3\text{H}_6 + \text{CO} + \text{H}_2\text{O} \quad \Delta H_{298} = +164 \text{ kJ} \cdot \text{mol}^{-1}
$$

(1)

$$
\text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2 \quad \Delta H_{298} = +124 \text{ kJ} \cdot \text{mol}^{-1}
$$

(2)

$$
\text{H}_2 + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H_{298} = +41 \text{ kJ} \cdot \text{mol}^{-1}
$$

(3)

$$
\text{CO}_2 + \text{C}_4 \rightarrow 2\text{CO} \quad \Delta H_{298} = +172 \text{ kJ} \cdot \text{mol}^{-1}
$$

(4)

$$
\text{C}_3\text{H}_8 + 3\text{CO}_2 \rightarrow 6\text{CO} + 4\text{H}_2 \quad \Delta H_{298} = +620 \text{ kJ} \cdot \text{mol}^{-1}
$$

(5)

$$
\text{C}_3\text{H}_8 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_4 \quad \Delta H_{298} = +82 \text{ kJ} \cdot \text{mol}^{-1}
$$

(6)

Even though the CO$_2$-ODHP reaction is an extremely challenging issue, many efforts have been devoted to the reaction, especially in developing highly efficient catalysts. To date (Nov. 10th, 2021), the number of published papers gradually increased and has reached up to 2702 based on the Web of Science from 2001 (Fig. 5). And there are some excellent reviews of the dehydrogenation of alkanes to alkenes elaborating the catalysts development, mechanism exploration, and energy analysis of the reaction, etc. For example, Weckhuysen et al. reviewed the dehydrogenation of light alkanes to summarize the nature of active sites, supports and promotes, reaction mechanism, and deactivation pathway of different catalytic systems [19]. Gong et al. described emerging technologies and catalyst development in DHP [9]. Yang et al. outlined the most promising catalysts in the selective dehydrogenation of light alkanes [8]. Hermans et al. reviewed the development of boron-based catalysts for alkane oxidative dehydrogenation [23]. There are also some reviews on CO$_2$ as a soft oxidant and promoter in oxidative dehydrogenation of light alkanes [35, 45, 48, 49]. In addition, Rownaghi et al. summarized the roles of promoter and support in CO$_2$ oxidative C–H bond scission in the absence and presence of CO$_2$ [50]. Chen et al. outlined relationship between the structure and performances in
achieving the reaction via diversified characterization methods [44]. Shi et al. also reviewed the nature of active sites and the roles of modifiers and supports for different types of catalysts in CO₂ oxidative dehydrogenation of light alkanes [51]. Besides, Wu et al. described the DHP with different soft oxidants (e.g., CO₂, N₂O, S-containing compounds, and halogens/halides) [33].

As mentioned above, the Cr-based catalysts are widely used in the reaction. However, they are toxic and harmful to the environment. The Cr-free catalysts play important roles in the development of CO₂-ODHP, and some of them have great potential applications in industry. However, no relative reviews are systematically generalized on the Cr-free catalysts. Based on our recent works on CO₂-ODHP, in this review, we focused on the Cr-free catalysts especially in the CO₂-ODHP reaction mainly reported within the last decade, including the structural information and the nature of active sites, catalytic performances, mechanisms of Cr-free catalytic systems, as well as the role of CO₂ in the reaction.

2 Catalysts in CO₂-assisted dehydrogenation of propane to propylene

For the CO₂-ODHP reaction, an effective catalyst not only needs to selectively activate the C–H bond with suppression of the C–C cleavage, but also has an affinity for CO₂ activation. As a typical acidic molecule, CO₂ is preferentially adsorbed on the active sites of catalysts, while propane prefers to be adsorbed on the acidic sites [44, 50]. Thus, a catalyst with suitable acidity and basicity is also a key factor to obtain satisfactory catalytic performance. To date, CrOₓ-based materials have been pointed out as the most promising catalysts in the CO₂-ODHP reaction for the high activity. It has been widely accepted that during the reaction, propane is dehydrogenated to propylene over tetrahedra Cr⁴⁺ sites, which is simultaneously reduced to octahedra Cr³⁺. The reduced Cr³⁺ can be re-oxidized to Cr⁴⁺ by CO₂, and thus complete a redox cycle [52]. At a low Cr content, the reduced Cr³⁺ can be migrated to form Cr₂O₃ clusters, which can be further reduced to Cr²⁺ by in situ generated H₂. The deeply reduced Cr²⁺ has a strong adsorption capacity to CO₂ and is re-oxidized to Cr³⁺ by CO₂. Simultaneously, CO is formed through the reduction of CO₂. Thus, the catalytic performances of CrOₓ-based catalysts are drastically affected by the Cr⁴⁺/Cr³⁺ ratio, which links to the dispersibility of Cr species and the interaction between the catalytic active sites and supports.

Recently, Liu et al. have successfully prepared a 2 wt% CrOₓ/Silicalite-1 catalyst with a high space–time yield of 16.7 kgₚropiclyne·h⁻¹·Cr⁻¹ for the CO₂-ODHP, which showed the highest activity among Cr₂O₃-based catalysts [53]. However, the inherent properties of Cr such as short lifetime and toxicity force researchers to seek alternative and sustainable catalytic systems. Takehira et al. [54] investigated the catalytic performances over different M-MCM-41 catalysts (M: V, Cr, Mn, Fe, Co, Ni and Ga) in the CO₂-ODHP and found that the activity followed the order of Cr > Ga > Ni > V > Fe > Mn > Co (Fig. 6). The results greatly encouraged researchers to further explore other catalytic systems with Cr-free. Nowadays, the typical catalysts with Cr-free for the CO₂-ODHP include the redox-type transition metal oxides (V, Ce, Mo, etc.), main group metals (Ga, In, etc.), and precious metals (Pt, Pd, Au, Rh, etc.). The expansion of catalytic systems ignites the hope of realizing the industrialization of CO₂-ODHP to offset the demand gap of propylene.

2.1 Redox-type metal oxide catalysts

2.1.1 Cerium-based rare metal catalysts

Generally, Ce-based material is a crucial component in three-way catalysts (TWCs) applied in the automobile exhaust gas due to its high oxygen-storage capacity (OSC) [55]. CeO₂ has oxidizing properties under an oxygen-poor or anoxic condition. Recently, it has been reported that Ce could effectively activate the dry reforming of alkanes and the oxidative dehydrogenation of ethylbenzene to styrene in the presence of CO₂. The catalytic activity was related to the facile realization of the Ce⁴⁺/Ce³⁺ redox cycle, which could also induce direct C=O bond scission of CO₂ to provide available lattice oxygen for selective oxidation and coke suppression. In addition, the results of in situ DRIFTS tests and the density functional theory (DFT) calculations
revealed that CO₂ could reactively adsorb on ceria to form carbonate and bicarbonate at low temperatures. Subsequently, they could be decomposed and desorbed at high temperatures to release available surface sites for ODH reaction [56, 57]. Therefore, the high OSC performance, excellent redox properties, and natural activation ability for CO₂ on Ce-based catalysts verify that they have a potential application in the CO₂-ODHP reaction.

Ji et al. employed SBA-15 as a support to prepare Ce-based monolithic catalyst for the CO₂-ODHE (E means ethane), which exhibited excellent performance with 63.9% conversion of ethane and 87.2% selectivity to ethylene at 750 °C [58]. They also revealed that Ce⁺⁴ species with a high oxidation state were the active sites, which could be reduced to Ce⁺³ species in dehydrogenation process and the reduced Ce⁺³ species were further re-oxidized to Ce⁺⁴ species by CO₂ at 750 °C. Subsequently, Djinović et al. [59] utilized an electron-rich active carbon (AC) to adjust the electron environment of CeO₂ and prepared a CeO₂/AC catalyst, which could achieve the CO₂-ODHP. The catalyst was found to be susceptible to the dehydrogenation of propane, and especially a catalyst with large CeO₂ size was beneficial for re-oxidation with CO₂. It is difficult to improve the performance of the sole CeO₂ in heterogeneous catalysis probably for the low specific surface area (S_{BET}) and single pore structure. Thus, the introduction of foreign metals into CeO₂ is an important method to adjust the electronic properties of CeO₂, improve the stability, and enrich the surface oxygen vacancies for achieving excellent catalytic activity [60–63]. Corberán et al. improved the catalytic performances of CO₂-ODHE via incorporating Ca species into the CeO₂ framework [64]. Wang et al. [65] dispersed Ni on the surface of CeO₂ to improve the amount of oxygen vacancies of CeO₂, resulting in excellent catalytic performances in RWGS reaction.

Even though the lattice oxygen plays an important role in catalysis, its strong oxidizing properties in CeO₂ can cause cracking and dry reforming of propane. In order to appropriately reduce the oxidizing capacity of the lattice oxygen in CeO₂, Wang and Tsilomelekis [66] introduced Fe into CeO₂ to obtain FeCeO₃ solid solution catalysts for the CO₂-ODHP and found that the selectivity of ODHP was enhanced at a high Fe/Ce ratio and cracking was suppressed. A 5FeCeO₃ catalyst exhibited the most stable catalytic behavior in a 20-h continuous test with 9.5% conversion of propane and 45% selectivity to propylene. In addition, the results of ex-situ Raman, XPS, and TEM revealed that the coke deposition was the main reason for deactivation of the catalyst with a low Fe/Ce ratio. For a catalyst with a high Fe content, the sintering of CeO₂ and the migration of Fe to form nanocrystals were the main reasons for the irreversible deactivation. The instability of the catalyst structure limits the further improvement of catalytic activity.

Nowicka et al. [67] introduced Zr and Al into CeO₂ to form a CeZrAlOₓ catalyst, which could increase the amount of potential oxygen vacancies and improve durability of the catalyst. Subsequently, Pd was impregnated onto the CeZrAlOₓ support (denoted as Pd/CeZrAlOₓ) to improve the redox characteristic of Ce species, which achieved the CO₂-ODHP reaction with 9.5% of propane conversion and 93% of propylene selectivity at 500 °C with a long-term stability. The DRIFTS analysis suggested that Pd could induce the dissociation of CO₂ on surface of the spent catalyst to form CO (Fig. 7b). Although the by-products of CO and H₂O were generated in Mars-van Krevelen (MvK) route and RWGS route, the former route did not require the stepwise formation of H₂ as an intermediate. Based on this point, they proposed that the MvK and RWGS mechanisms could be linked with Ce-based catalysts, namely lattice oxygen adsorbed hydrogen of alkane molecules to form alkene and H₂O, while CO₂ replenished these oxygen species through Pd, releasing CO into the gas phase. At the same time, the in situ H₂ generated from the dehydrogenation of propane was consumed by CO₂ via the RWGS reaction, resulting in shifting the equilibrium of alkane dehydrogenation (Fig. 7a).

Besides, the oxygen vacancy of CeO₂ possesses the ability of dissociation of CO₂ to CO and lattice oxygen. The lattice oxygen of CeO₂ can maintain precious metals in a highly oxidized state, resulting in improving the dehydrogenation performance of alkane. In addition, the bimetallic alloys can modify the surface d-band center and change the adsorption energies of reactants and intermediates, resulting in different catalytic performances. For example, Chen et al. prepared several bimetallic catalysts supported on CeO₂ (such as CoPt/CeO₂, CoMo/CeO₂, NiMo/CeO₂, and NiFe/CeO₂) for the reactions of reforming and CO₂-ODHE [68]. The DFT calculated energy profiles on CoPt/CeO₂ and NiFe/CeO₂ confirmed that the C–C bond cleavage of ethane to CH₃*, CO*, and H₂O(g) was exothermic on Pt-terminated CoPt(111) leading to enhancement for the reforming reaction to produce syngas (Fig. 8a). Contrarily, the pathway for selective C–H bond cleavage was more energetically favorable on the mixed NiFe(111) surface, leading to the improvement of selectivity of ODHE (Fig. 8b). Subsequently, the same group investigated the effect of Ni/Fe molar ratios of NiFe/CeO₂ catalysts for the CO₂-ODHP and the CO₂-ODHE [21, 69–71]. They found that the product distribution could be adjusted by changing the amount of Fe. A small amount of Fe (NiₓFe₁₋ₓ) was beneficial to forming syngas, while an optimal amount of Fe (NiₓFe₁₋ₓ) greatly increased the selectivity to alkene. The in situ characterization and DFT calculations revealed that the NiFe₃ was composed of
oxidized Fe and metallic Ni, and the Ni-FeO \textsubscript{X} interfacial sites could selectively break the C–H bonds but preserve the C–C bonds of alkene to improve the selectivity to alkene. Different from the Ni-FeO \textsubscript{X} catalyst, the Ni-CeO \textsubscript{X} interfacial sites could efficiently cleave all of the C–H and C–C bonds to produce syngas. Thus, controlled synthesis of the two distinct active sites could enable rational enhancement of the alkene selectivity in the CO\textsubscript{2}-ODHP and the CO\textsubscript{2}-ODHE.

In summary, the catalytic performance of the CO\textsubscript{2}-ODHP over Ce-based catalysts is generally determined by the rate of the Ce\textsuperscript{4+}/Ce\textsuperscript{3+} redox cycle, which is related to the amount and stability of lattice oxygen in the catalysts. Generally, the construction of a solid solution can improve the stability of Ce-based catalysts. Besides, introducing a foreign metal on the surface of CeO\textsubscript{2} to create an interfacial effect can also improve theCe\textsuperscript{4+}/Ce\textsuperscript{3+} redox cycle, resulting in an improvement of catalytic performance. Although Ce-based catalysts have exhibited promising results, there are still many difficulties must be overcome for obtaining a higher catalytic activity than that of Cr-based catalysts.

2.1.2 Vanadium-based catalysts

V-based material is one of the most promising alternatives to Pt- and CrO\textsubscript{X}-based catalysts in ODHP. Kondratenko et al. compared the catalytic performances of a VO\textsubscript{X}/MCM-41 catalyst possessing highly dispersed VO\textsubscript{X} species with industrially relevant CrO\textsubscript{X}/MCM-41 and Pt–Sn/Al\textsubscript{2}O\textsubscript{3} catalysts [72]. They found that the former catalyst exhibited a higher propylene selectivity and better stability during several cycles of the dehydrogenation of propane and oxidative regeneration. And the formation of carbon
deposits was the main reason for the deactivation of the VO\textsubscript{2}/MCM-41. In addition, according to the type of supports, VO\textsubscript{x} could appear in multiple forms including monomeric, oligovanadate, polymeric, and crystalline V\textsubscript{2}O\textsubscript{5}. Among them, the monomeric and the oligovanadate were beneficial to the formation of C\textsubscript{3}H\textsubscript{2} from the vanadium components could be polymerized by Sauer et al. via DFT calculations and microkinetic simulations [82]. For example, Galvita et al. found that the agglomeration of the VO\textsubscript{x} species in a WO\textsubscript{x}-VO\textsubscript{2}/SiO\textsubscript{2} catalyst could be hindered since WO\textsubscript{x} acted as a physical barrier to the VO\textsubscript{x} species [83]. Moreover, a control experiment of adding D\textsubscript{2} into the C\textsubscript{3}H\textsubscript{8} and CO\textsubscript{2} feed gases confirmed that the reaction followed ODHP and RWGS. Besides, the structural and catalytic performances of V-based catalysts are also improved by employing a promoter. It has been proved that there is no interaction between dissimilar metal (Cr, Mo, W, etc.) oxides and VO\textsubscript{x}, but they only act as physical barriers to prevent the polymerization of VO\textsubscript{x} [82]. For example, Galvita et al. found that the agglomeration of the VO\textsubscript{x} species in a WO\textsubscript{x}-VO\textsubscript{2}/SiO\textsubscript{2} catalyst could be hindered since WO\textsubscript{x} acted as a physical barrier to the VO\textsubscript{x} species [83]. Moreover, a control experiment of adding D\textsubscript{2} into the C\textsubscript{3}H\textsubscript{8} and CO\textsubscript{2} feed gases confirmed that the reaction followed ODHP and was accompanied by the RWGS (Fig. 10). Combined with DFT calculations, they confirmed that the CO\textsubscript{2}-ODHP occurred at the isolated O=V\textsuperscript{5+}–O–V\textsuperscript{3+} sites. However, the reduced V\textsuperscript{4+} active sites also played an important role in activating and extracting the second C–H bond of C\textsubscript{3}H\textsubscript{8}. However, they proposed two reaction pathways that were probably involved in the reaction over the O=V\textsuperscript{5+}–O–V\textsuperscript{3+} sites, i.e., the direct ODHP pathway and the coupling DHP and the RWGS pathway. In the former pathway, C\textsubscript{3}H\textsubscript{8} could be oxidized by the O=V\textsuperscript{5+}–O–V\textsuperscript{3+} sites to produce C\textsubscript{3}H\textsubscript{6} and H\textsubscript{2}O, and O=V\textsuperscript{3+}–O–V\textsuperscript{3+}
sites were simultaneously generated as well, which was immediately re-oxidized by CO\textsubscript{2} to O=V\textsuperscript{5+-O-V\textsuperscript{3+}} sites. CO\textsubscript{2} was converted to CO. However, the coupling of DHP and RWGS pathway followed two steps. At first, DHP occurred over the O=V\textsuperscript{5+-O-V\textsuperscript{3+}} sites to produce C\textsubscript{3}H\textsubscript{6} and H\textsubscript{2}, and then, the partial H\textsubscript{2} could reduce the O=V\textsuperscript{5+-O-V\textsuperscript{3+}} sites to the O=V\textsuperscript{3+-O-V\textsuperscript{3+}} sites, which were re-oxidized by CO\textsubscript{2} to the O=V\textsuperscript{5+-O-V\textsuperscript{3+}} sites and CO. A similar pathway was confirmed by Hess et al. using operando UV Raman spectroscopy [84, 85]. They observed distinct changes of the surface V species involving the breakage of V-O-V bonds, a partial reduction in vanadyl, as well as the formation of support hydroxyl groups.

Generally, vanadium oxide can form vanadate with alkali metals. Guliants et al. varied the surface coverage of VO\textsubscript{x} species by using sodium on the silica surface [86]. They found that Na\textsuperscript{+} could significantly improve the dispersion of surface VO\textsubscript{x} species and resulted in the formation of surface Na-metavanadate. Subsequently, Hossain et al. introduced La\textsubscript{2}O\textsubscript{3} into Al\textsubscript{2}O\textsubscript{3} supports to obtain a VO\textsubscript{x}/La\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3} catalyst for the CO\textsubscript{2}-ODHP [87]. They found that the introduction of La decreased the reducibility
and total acidity of the catalyst, resulting in an improvement of propylene selectivity. CO₂ can act as a mild oxidant in direct interaction with the hydrocarbons and re-oxidize the reduced catalysts while masking the non-selective sites of the catalysts to enhance olefins selectivity. In addition, the anti-coke formation performance of V-based catalysts can be enhanced by 3D printing which can considerably modify the surface properties and bulk oxide phase dispersion, thus leading to enhanced metal oxide reducibility and exceptional CO₂-ODHP performance [88–90].

Compared with Cr-based catalysts, V-based catalysts possess excellent catalytic performances and suppressed deactivation rates. However, the redox ability of V species depends primarily on the dispersion which can be adjusted by promoter, support, and the preparation method, further resulting in different performances. In addition, the rich V species including V⁵⁺, V⁴⁺, V³⁺, isolated V, oligomeric Vⁿ⁺, and crystalline V₂O₅ make the identification of active species very difficult. Thus, the design strategy should consider many factors simultaneously to obtain an effectively V-based catalyst for industrial application of CO₂-ODHP.

2.2 Main group metal-based catalysts

2.2.1 Gallium-based catalysts

Along with Cr- and V-based catalysts, Ga-based catalysts have been recognized as another important catalytic system for the CO₂-ODHP since the Ga₂O₃/TiO₂ catalyst was established in achieving the CO₂-ODHE [50, 91]. Subsequently, Michorczyk and Ogonowski [92] found that the bulk Ga₂O₃ catalyst was more effective for the CO₂-ODHP than the bulk Cr₂O₃ and Fe₂O₃ catalysts. The bulk Ga₂O₃ provided a propylene yield of 30.1% at 600 °C, which was greater than the 10% yield obtained over the bulk Cr₂O₃ and Fe₂O₃. Subsequently, they successfully enhanced the initial activity and stability of the catalyst by adding K to Ga₂O₃ catalyst [93]. There are five polymorphs of α-, β-, γ-, δ-, and ε-Ga₂O₃, and all of them were widely investigated in the CO₂-ODHP [94]. Among them, the β-Ga₂O₃ exhibited the highest catalytic activity for the abundant of coordinatively unsaturated Ga³⁺ cations and the conjugated effect of H and O on surface [94]. Meanwhile, they also revealed that the reaction occurred via the heterolytic dissociation of propane over Ga₂O₃ and CO₂ promoted the reaction via the RWGS and the reverse Boudouard reaction. However, the low surface area lowered catalytic performance over the β-Ga₂O₃. Cao et al. successfully prepared a mesoporous β-Ga₂O₃ with a high surface area by employing eco-friendly sucrose as the non-surfactant template and applied it in catalyzing the CO₂-ODHP [95]. The conversion of propane was approximately twofold higher than that over the conventional mesoporous-free β-Ga₂O₃, attributed to the improved textural structure providing a high abundance of coordinative unsaturated surface Ga sites. Meanwhile, Michorczyk et al. [96] synthesized a thermally stable mesoporous Ga₂O₃ with the pore size and surface areas in the ranges of 6.2–6.5 nm and 231–322 m²·g⁻¹ by the nanocasting approach. Compared with the Ga₂O₃ prepared without a hard template, the mesoporous Ga₂O₃ exerted a higher resistance on deactivation during the CO₂-ODHP reaction.

Normally, the activity of Ga-based catalysts is determined by the coordination state which is affected by the nature of support. The acidity and basicity also affect the catalytic performances remarkably. Yue et al. investigated the effects of support on the catalytic performances in the CO₂-ODHP over the Ga₂O₃ loaded on differential supports such as TiO₂, Al₂O₃, ZrO₂, SiO₂, and MgO [97, 98]. The Ga₂O₃/TiO₂, Ga₂O₃/Al₂O₃, and Ga₂O₃/ZrO₂ catalysts offered high catalytic activities for their abundant medium-strong acidic sites (Fig. 11). Especially, the Ga₂O₃/TiO₂ catalyst with a strong interaction between TiO₂ and Ga₂O₃ possessed abundant reduced Ga⁷⁺ (δ < 2) offered the highest conversion of propane (32%). Due to un-reduction of Ga₂O₃ under reaction temperature, the dehydrogenation of propane proceeded via a heterolytic dissociation step, namely propane was activated on Ga₂O₃ active sites via the heterolytically dissociative adsorption, forming Ga–H and Ga–OR species, and the latter was further decomposed to products [97, 99]. Subsequently, Cao et al. found that the structure of spinel-type Ga₂O₃-Al₂O₃ solid solutions was beneficial to the dispersion of surface Ga sites which formed the abundant weak acidic sites and tetrahedral Ga³⁺ cations, resulting in a high activity and stability in the CO₂-ODHP [100, 101]. To improve the stability of Ga₂O₃-Al₂O₃ catalysts, Michorczyk et al. [96] prepared mesoporous Ga₂O₃-Al₂O₃ oxides with pore architecture similar to SBA-15, which exhibited a promising catalytic performance and stability in the CO₂-ODHP. Tan et al. prepared Ga₂O₃-Al₂O₃ catalysts by a hydrothermal method, which gave 35.2% conversion of propane and 95.0% selectivity to propylene in the CO₂-ODHP [102]. The characterization results revealed that the high surface area of Ga₂O₃-Al₂O₃ possessed a large amount of tetrahedral Ga ions (e.g., Ga³⁺ and Ga⁷⁺, δ < 2) related to medium-strong Lewis acidic sites, resulting in a superior catalytic activity.

Furthermore, zeolites are usually employed as supports for building bifunctional Ga-based catalysts applied in propane aromatization, in which the Ga sites catalyze dehydrogenation of propane and the Brønsted acidic sites are responsible for the aromatization of propylene [103–105]. Thus, it is appropriate to reduce the amount of Brønsted acid sites to adjust the product distribution in the CO₂-ODHP. Yue et al. adjusted the acidity of the Ga₂O₃/
HZSM-5 catalysts through dealumination of the HZSM-5 and achieved a 22% yield of propylene without observable deactivation in 100 h [106, 107]. After that, the same group introduced phosphorus into HZSM-5 to decrease the acid strength and strong acid sites of the Ga2O3/HZSM-5 catalyst, resulting in an improvement of stability [108]. Subsequently, they employed ZSM-48 as a support to prepare Ga2O3/ZSM-48 catalysts, which exhibited a higher propylene selectivity in the CO2-ODHP than over the Ga2O3/HZSM-5. The improved selectivity resulted from the high Si-containing zeolite with a weaker acid strength than ZSM-5 [109]. At the same time, they also improved the propylene selectivity by replacing the ZSM-5 with MWW-type zeolites of ITQ-2 and MCM-22. The ITQ-2 showed a more open pore structure but a lower amount of strong Brønsted acid sites. After loading Ga2O3, Ga2O3/ITQ-2 provided a higher propylene selectivity and better stability for the CO2-ODHP than Ga2O3/ZSM-5 catalysts [110]. Furtherly, Orlyk et al. [111] used dealuminated BEA zeolite (SiBEA) as support with adjustable acidic-basic and redox properties to obtain Ga,SiBEA catalysts. They could achieve the CO2-ODHP with a 40% yield of propylene due to the formation of Lewis acid sites by isolated GaIII sites. Agafonov et al. [112] found that the silanol nests of SiO2 could enhance the dispersion of active Ga species and the SiO2 with low acidity could prevent coke deposition to improve the stability of the catalyst in the CO2-ODHP. Yue et al. also found that in Ga2O3/NaZSM-5 catalysts, silanol nests were helpful in dispersing active species of GaOx and could act as Brønsted acidic sites to produce conjugation effects with Ga species to promote the dehydrogenation reaction [113]. Lercher et al. verified the synergetic interaction between Ga+ and Brønsted acid sites, namely the protons were able to exchange with Ga+ to improve the activity of dehydrogenation [114]. However, a high Ga content could promote the formation of Ga2O3 clusters, resulting in low catalytic activity. In addition, the highest reaction rates in propane dehydrogenation could be achieved at equal concentrations of Brønsted and Lewis acid Ga+ sites for the synergy effect between them [115].

In most Ga-zeolite systems, it has been proved that there are many types of Ga species such as isolated Ga3+, Ga5+ (\(\delta < 2\)), [GaO]+, [Ga(OH)]2+, [Ga(OH)2]3+, [GaH]2+, [GaH]2+, and [Ga2O3]3+ on framework or extra-framework of the zeolites, which possessed different capabilities for the activation of C–H bonds in propane. Fan et al. used DFT calculation to study the propane dehydrogenation over perfect Ga2O3(100) and revealed the high energy barrier of surface hydroxyl groups of [Ga(OH)]2+ and [Ga(OH)2]+, which were difficult to form H2 and H2O.
resulting in further dehydrogenation or oligomerization of adsorbed propylene [99]. In addition, the formation of [GaH]^{2+} over Ga_{2}O_{3} is regarded as a rate-determining step in propane dehydrogenation. Lercher et al. also combined DFT calculations and experiment data and finally found that Ga^{+} could be protonated by a Brønsted acidic site to form a strong Lewis acidic site of [GaH]^{2+}, which was synergic with framework oxygen of the Brønsted acidic site to heterolytically cleave C–H bonds of propane with a very low intrinsic enthalpy barrier of 56 kJ mol^{-1} [114]. Meanwhile, Bell et al. utilized the free energy landscapes of all of the reactions to establish the nature of the active Ga species such as [GaH]^{2+}, [GaH_{2}]^{+}, and [Ga]^{+}, as well as the associated dehydrogenation mechanism [116]. It was found that compared to other Ga species, [GaH]^{2+} was the most active site for the dehydrogenation of light alkane. Under the catalyzing of [GaH]^{2+}, the ΔH value for transition states (TSs) formation decreased with increasing the carbon number in light alkene (Fig. 12).

Besides the common metal oxides, GaN constitutes another potential heterogeneous catalyst for oxidative dehydrogenation of propane [30, 32, 117–120]. Inspired by the special strong local electrostatic polarization of GaN [121–125], recently, our group developed several GaN-based catalysts for C–H bond activation in the CO_{2}-ODHP reaction [47, 126–128]. For example, Q-x (a type of SiO_{2} supports with varying pore size) as supports to prepare GaN/Q-x catalysts which exhibited good to excellent catalytic activity and reusability in CO_{2}-ODHP. It was also found that CO_{2} played a positive role in inhibiting carbon deposition on surface of the catalyst during the reaction (Fig. 13a, b). However, an obviously long induction period was required. Subsequently, we replaced Q-x with commercial NaZSM-5 to synthesize GaN/NaZSM-5 catalysts with an initial propane conversion of 45.0% and propylene yield of 28.3% at 600 °C and found that the strong acidic sites of NaZSM-5 were beneficial to the dispersion of GaN. And the strong interaction between GaN and the NaZSM-5 support contributed to the formation of Si–O–GaN species, which reacted with propane to form Si–O–GaN–H species, and CO_{2} further reacted with Si–O–GaN–H to form the *COOH intermediate and then release propylene, CO, and the Si–O–GaN active site (Fig. 13c–g). Based on the experimental results, we proposed the coupling of DHP and RWGS mechanism, namely DHP path occurred over Ga species to form C_{3}H_{6} and H_{2}, and then, the in situ

![Fig. 12 Ethane dehydrogenation via different mechanisms over different Ga species at 823 K and 1.01 x 10^5 Pa, a alkyl mechanism (cyclic route) on [GaH]^{2+}; b stepwise alkyl mechanism on [GaH_{2}]^{+}; c alkyl mechanism on Ga^{+}; d effects of increasing chain length and substitution on light alkene formation TSs in alkyl light alkane dehydrogenation mechanism on [GaH]^{2+}. Reproduced with permission from Ref. [116]. Copyright 2018, American Chemical Society](image-url)
produced H₂ was consumed via RWGS to produce CO and H₂O, resulting in the equilibrium of DHP shifting toward propylene formation (Fig. 13h).

For the non-redox Ga-based catalysts, the CO₂-ODHP reaction follows the mechanism of two-step non-oxidative routes, namely the step of direct dehydrogenation of propane and the step of RWGS. The combination of these two steps results in the reaction equilibrium shifts to the production of propylene. Therefore, it is practicable to employ zeolite to build bifunctional catalysts with Ga for CO₂-ODHP. In terms of C–H bond activation, propane is usually heterolytically dissociative on Ga species to form Ga-hydride and Ga-alkoxy species. Thus, it is necessary to select promoters or heteroatom to adjust the electronic structure of Ga to achieve excellent catalytic performances. In addition, the thermal stability and hydrophobicity of support such as zeolite also need to be considered for industrial application.

### 2.2.2 Indium-based catalysts

Indium, as an element similar to Ga in the IIIA group, has also been widely investigated in the CO₂-ODHP. In practical terms, the catalysts of indium oxide in combination with zeolites or Al₂O₃ have been applied in de-NOₓ reactions due to the good redox characteristics of indium species [129, 130]. In terms of the CO₂-ODHP reaction, Cao et al. studied the effects of foreign metals in the metal...
oxide of In$_2$O$_3$-MO$_x$ (M = Al, Zn, Zr, Ti, Fe, Mg, Si and Ce) on the catalytic performances of the CO$_2$-ODHP [131]. They found that In$_2$O$_3$-Al$_2$O$_3$ catalyst showed the highest activity and superior long-term stability for the higher redox property derived from the interaction between In$_2$O$_3$ and Al$_2$O$_3$. Then, they investigated the effects of acid–base properties of Al$_2$O$_3$, ZrO$_2$, and SiO$_2$ supports and the interactions between these supports with In$_2$O$_3$ on the performances for the reaction. It was found that the high-intensity basic sites on the In$_2$O$_3$-ZrO$_2$ catalyst remarkably promoted the RWGS reaction. The high dispersion of In$_2$O$_3$ and balanced acid/base properties in the In$_2$O$_3$-Al$_2$O$_3$ catalyst resulted in superior catalytic performance in the CO$_2$-ODHP [132]. Unlike Ga-based catalysts, the excellent redox characteristics of In$_2$O$_3$ make it possible to be reduced to In$^0$, which cannot be re-oxidized by CO$_2$ [132, 133]. Thus, the CO$_2$-ODHP reaction over In-based catalysts also follows the mechanism of two-step non-oxidative routes. Cao et al. investigated the In$_2$O$_3$-Al$_2$O$_3$ bimetallic oxide in the CO$_2$-ODHP and confirmed that the combination of the two components was beneficial for the dispersion of In$_2$O$_3$ and formation of In–Al–O species with high reducibility. They proposed that the metallic In$^0$ species was crucial for the dehydrogenation, and basic sites of Al$_2$O$_3$ were responsible for the activation of CO$_2$ to promote the RWGS reaction [133, 134]. In addition, Ma et al. found that there was no induction period over In/HZSM-5 catalyst in the CO$_2$-ODHP reaction, at the same time, the formation of In$^0$ would lead to a decrease in activity of In/HZSM-5 [135]. Thus, they considered that In$^{3+}$ was the main active species, which promoted not only the DHP but also RWGS in the CO$_2$-ODHP reaction (Fig. 14).

The CO$_2$-ODHP reaction follows the mechanism of the two-step non-oxidative routes over In-based catalysts despite the fact that In shows excellent redox characteristics. And the dispersion that In$_2$O$_3$ and acid–base properties of supports are crucial to achieving the CO$_2$-ODHP. Nevertheless, the identification of active species is still an important issue in In-based catalysts.

2.3 Precious metal (Pt, Rh, Ru, and Pd) catalysts

Precious metals such as Pt, Ru, Rh, Pd, and Au are also applied in the DHP reaction [8]. Among these reported precious metals, Pt-based catalysts have been successfully applied in the industrial Oleflex technology of the DHP. Many strategies were adopted to reduce Pt loading, improve stability, and resist sintering and carbon deposition [10, 136–140].

For the CO$_2$-ODHP reaction, it is worth noting that the Pt-based catalyst can cleave both of the C–H and C–C bonds of propane. Thus, the products contain a large amount of syngas (CO and H$_2$) [71, 141]. To improve the selectivity of propane dehydrogenation to propylene, tandem catalysts could be applied. For example, recently, Notestein et al. successfully created nanoscale tandem catalysts by growing a 2-nm shell of In$_2$O$_3$ over Pt/Al$_2$O$_3$ for the ODHP, in which Pt NPs were used for the propane dehydrogenation and the interface between In$_2$O$_3$ and Pt was responsible for oxidizing surface H atoms to water.

Fig. 14 Reaction processes for CO$_2$-ODHP over In$_2$O$_3$/HZSM-5. Reproduced with permission from Ref. [135]. Copyright 2020, Wiley–VCH.
This approach minimized coking and improved the yield of propylene up to 30%.

Simultaneously, McFarland et al. compared the catalytic activity and stability of Ru loaded on CeO$_2$ and ZrO$_2$ catalysts for the CO$_2$ partial oxidation of propane [60]. They found that the excellent activity for the C–C cleavage was conducted over Ru even neither catalyst showed measurable activity for the CO$_2$-ODHP to propylene. O’Brien et al. enhanced the yield of propylene in the CO$_2$-ODHP for twofold over 1 wt% Ru modified the conventional Cr$_2$O$_3$/SiO$_2$ catalyst than over the ruthenium-free catalyst [143]. They found that a small amount of Ru promoted the activation of CO$_2$ and removed the adsorbed H$_2$ on the catalyst surface via RWGS to shift the equilibrium of reaction to produce propylene, resulting in an increase in the activity without breaking the C–C bonds.

Solymosi and Tolmacsov [141] have proved that the activities of Pt-, Ru-, Rh-, and Pd-based catalysts for the CO$_2$ reforming of propane followed the order of Rh $>$ Ru $>$ Pt $>$ Pd. Subsequently, they investigated the adsorption, decomposition, and reaction of propane with CO$_2$ over Rh loaded on various supports (Al$_2$O$_3$, SiO$_2$, TiO$_2$, and MgO). The propane could interact with Rh sites to form propylene with selectivity ranges of 50%–60% at 824–923 K [144].

In addition, Pd-based catalysts are also positive for the CO$_2$-ODHP, which can promote both the reduction and reoxidation of the support and activate CO$_2$ [67]. Recently, the dehydrogenation of light alkanes could be conducted via the photocatalysis route under mild conditions (Fig. 15). Liang et al. reported a photocatalytic CO$_2$-ODHE over Pd/TiO$_2$ catalysts at room temperature [145]. CO$_2$ could be activated over Pd NPs to significantly promote the production of C$_2$H$_4$ and syngas, and a 1 wt% Pd/TiO$_2$ catalyst exhibited C$_2$H$_4$ and syngas production rates of 230.5 and 282.6 $\mu$mol g$_{\text{cat}}^{-1}$ h$^{-1}$, respectively. The intermediate energy level at the 3d orbital of Pd and the electron channel at the Pd–O covalent bonding over the Pd/TiO$_2$ catalyst facilitated the electron transfer, excitation, and separation, and finally achieved the reaction to form ethylene, CO, and H$_2$.

Despite these reported precious metal catalysts being active for the CO$_2$-ODHP reaction, their defects of expensive, sensitive, easy to be deposited with carbon and sinter, etc., make them rarely applied in the reaction.

Besides, Solymosi et al. also studied the product distribution of the CO$_2$-ODHP over Au deposited on ZnO, MgO, and Al$_2$O$_3$, respectively [146]. The propane conversion and propylene selectivity over the Au/ZnO were approximately 17% and 56%, respectively. CO$_2$ had a significant promoting effect for the reaction over the Au/ZnO catalyst due to the electronic interaction between the n-type ZnO and Au particles. Besides the oxidative dehydrogenation and dry reforming reaction, the decomposition of C$_3$H$_8$ and surface carbon deposition could also be observed.

In addition, Pt-based catalysts are also positive for the CO$_2$-ODHP, which can promote both the reduction and reoxidation of the support and activate CO$_2$ [67]. Recently, the dehydrogenation of light alkanes could be conducted via the photocatalysis route under mild conditions (Fig. 15). Liang et al. reported a photocatalytic CO$_2$-ODHE over Pd/TiO$_2$ catalysts at room temperature [145]. CO$_2$ could be activated over Pd NPs to significantly promote the production of C$_2$H$_4$ and syngas, and a 1 wt% Pd/TiO$_2$ catalyst exhibited C$_2$H$_4$ and syngas production rates of 230.5 and 282.6 $\mu$mol g$_{\text{cat}}^{-1}$ h$^{-1}$, respectively. The intermediate energy level at the 3d orbital of Pd and the electron channel at the Pd–O covalent bonding over the Pd/TiO$_2$ catalyst facilitated the electron transfer, excitation, and separation, and finally achieved the reaction to form ethylene, CO, and H$_2$.

Despite these reported precious metal catalysts being active for the CO$_2$-ODHP reaction, their defects of expensive, sensitive, easy to be deposited with carbon and sinter, etc., make them rarely applied in the reaction.

### 2.4 Other catalysts

In addition to the catalytic system mentioned above, there are other catalysts such as Mo-, Zn-, Fe-, and Zr-based catalysts used in the CO$_2$-ODHP with differential catalytic performances.

**Fig. 15** Possible reaction mechanism for photocatalytic ODE with CO$_2$ over Pd/TiO$_2$ catalyst. Reproduced with permission from Ref. [145]. Copyright 2018, American Chemical Society
### Table 2 Summary of catalytic data of various Cr-free catalysts used in CO$_2$-ODHP reaction

| Entry | Catalysts | $T$/°C | Flow/ml | Components | Conversion/% | $C_3$H$_6$ selectivity/% | $k_d$/h$^{-1}$ | Refs. |
|-------|------------|--------|---------|------------|-------------|-------------------------|--------------|-------|
| 1     | 5GaN/Q-3   | 600    | 30      | $C_3H_8/CO_2/N_2 = 1/2/7$ | –           | 31–21                   | 71–93        | 0.036 | [47] |
| 2     | 30CeVO$_4$/AC | 550    | 30      | $C_3H_8/CO_2/He = 1/1/1$ | 8.4         | 15–10                   | 42–49        | 0.119 | [59] |
| 3     | 10Fe$_3$CeO$_2$ | 550    | 20      | $C_3H_8/CO_2/N_2 = 1/1/18$ | 14          | 17–14                   | 48–55        | 0.013 | [66] |
| 4     | 5Pd/CeZrAlO$_x$ | 500    | 15      | $C_3H_8/CO_2/N_2 = 2/2/1$ | –           | 16–2                    | 80–91        | 0.015 | [67] |
| 5     | Fe$_3$Ni$_3$/CeO$_2$ | 550    | 10      | $C_3H_8/CO_2/Ar = 1/1/2$ | 4.0         | 4–2                     | 30–58        | 0.033 | [71] |
| 6     | VO$_2$/OAC  | 600    | 30      | $C_3H_8/CO_2 = 1/5$ | –           | 13.7                    | 60           | –     | [74] |
| 7     | nV-MSNS    | 600    | 15      | $C_3H_8/CO_2/Ar = 1/4/4$ | 10          | 58–33                   | 82–91        | 0.489 | [79] |
| 8     | nV-MCM-41  | 600    | 15      | $C_3H_8/CO_2/Ar = 1/4/4$ | 10          | 58–33                   | 88–93        | 0.527 | [81] |
| 9     | 7V5Mo/Al$_2$O$_3$ | 550    | 16      | $C_3H_8/CO_2/N_2 = 1/3/4$ | 3.3         | 10                      | 97           | –     | [82] |
| 10    | VO$_2$/SiO$_2$ | 550    | 16      | $C_3H_8/CO_2/Ar = 1/2/7$ | –           | 25                      | 45           | –     | [86] |
| 11    | VO$_x$/γ-Al$_2$O$_3$ | 600    | 6       | $C_3H_8/CO_2/Ar = 1/2/3$ | –           | 61                      | 70           | –     | [87] |
| 12    | 15V/ZSM-5  | 550    | 60      | $C_3H_8/CO_2/N_2 = 1/2/37$ | 45          | 35                      | 96           | –     | [88] |
| 13    | 15V-15Zr/ZSM-5 | 550    | 60      | $C_3H_8/CO_2/N_2 = 1/2/37$ | 44          | 35                      | 87           | –     | [89] |
| 14    | Cr$_{0.7}$Ga$_{1.1}$V$_{1.1}$Zr$_{1.1}$/ZSM-5(280) | 550    | 60      | $C_3H_8/CO_2/N_2 = 1/2/37$ | –           | 42                      | 91           | –     | [90] |
| 15    | Mesoporous β-Ga$_2$O$_3$ | 500    | 10      | $C_3H_8/CO_2/N_2 = 1/2/37$ | –           | 43–25                   | 89–95        | 0.102 | [95] |
| 16    | Mesoporous Ga$_2$O$_3$/Al$_2$O$_3$(4/1) | 550    | 30      | $C_3H_8/CO_2/He = 1/5/9$ | –           | 19–13                   | 92–95        | 0.113 | [96] |
| 17    | Hydrothermal Ga$_2$O$_3$/Al$_2$O$_3$ | 550    | 15      | $C_3H_8/CO_2/N_2 = 1/3/27$ | –           | 35–13                   | 96–97        | 0.148 | [102] |
| 18    | Ga$_2$O$_3$/HZSM-48(130) | 600    | 40      | $C_3H_8/CO_2/N_2 = 1/2/27$ | –           | 53–48                   | 42–46        | 0.018 | [109] |
| 19    | Ga$_2$O$_3$/ITQ-2 | 600    | 20      | $C_3H_8/CO_2/N_2 = 1/2/27$ | –           | 30–21                   | 72–78        | 0.064 | [110] |
| 20    | Ga$_2$SiBEA | 600    | 30      | $C_3H_8/CO_2/N_2 = 1/4/95$ | –           | 66.0                    | 63           | –     | [111] |
| 21    | 5GaN/ZSM-5(470) | 600    | 30      | $C_3H_8/CO_2/N_2 = 1/2/7$ | –           | 45–35                   | 63–78        | 0.044 | [126] |
| 22    | In$_2$O$_3$/Al$_2$O$_3$/20 | 600    | 10      | $C_3H_8/CO_2/N_2 = 1/4/95$ | –           | 36–29                   | 77           | 0.058 | [131] |
| 23    | In$_2$O$_3$/ZrO$_2$/10 | 600    | 10      | $C_3H_8/CO_2/N_2 = 1/4/95$ | –           | 26–20                   | 24–64        | 0.043 | [132] |
| 24    | In$_2$O$_3$/Al$_2$O$_3$/20-alcoholic | 600    | 10      | $C_3H_8/CO_2/N_2 = 1/4/95$ | 4–10        | 27–37                   | 18–76        | –     | [133] |
| 25    | 12 wt%In$_2$O$_3$/HZSM-5 | 580    | 20      | $C_3H_8/CO_2/N_2 = 1/4/5$ | 2–6         | 25–18                   | 79–65        | 0.084 | [135] |
| 26    | Ru$_{15}$Cr$_{10}$O$_{5}$/SiO$_2$ | 500    | 30      | $C_3H_8/CO_2/N_2 = 1/1/1$ | 6–4         | 25–18                   | 79–65        | 0.092 | [143] |
| 27    | MoO$_3$/La$_2$O$_3$/γ-Al$_2$O$_3$(1:2) | 550    | 6       | $C_3H_8/CO_2 = 1/1$ | –           | 56                      | 63           | –     | [149] |
| 28    | 5 wt%ZnO/HZSM-5(480) | 600    | 20      | $C_3H_8/CO_2/N_2 = 1/2/27$ | –           | 41–26                   | 68–74        | 0.024 | [155] |

*The best catalyst in References
*Molar ratio
$^c_{k_d}$: deactivation rate constant calculated from $\ln((1-X_{\text{final}})/X_{\text{initial}}) = k_d t + \ln((1-X_{\text{final}})/X_{\text{initial}})$, where $X$ means propane conversion.
Similar to Cr-, V-, and Ce-based catalysts, Mo-based catalysts possess multiple oxidation states and are also potential in the CO2-ODHP. For instance, Gaigneaux et al. confirmed that a NiMoO4 catalyst showed interesting catalytic performances, and CO2 could be dissociated over the catalyst to form adsorbed oxygen species, which could participate in the reaction to enhance the conversion of propane [147, 148]. Generally, the terminal M=O bonds of molybdenum oxide can abstract H atom from the methylene group to form a surface hydroxyl group, and an adsorbed iso-propyl can be eliminated as a hydride to generate propylene and a second hydroxyl group. Meanwhile, the molybdenum oxide species were recovered and the by-product of water was formed [29]. Hossain et al. studied the CO2-ODHP reaction catalyzed by MoO3/La2O3/γ-Al2O3 catalysts. The incorporation of La2O3 into γ-Al2O3 could improve the selectivity to olefins via moderating the surface acidity of the catalyst. Moreover, CO2 could partially re-oxidize the reduced active sites, resulting in an enhancement of overall performances in the CO2-ODHP [149]. In short, the special redox properties of Mo-based catalysts are conducive to the proceeding of the CO2-ODHP, implying they possess potential application in the reaction. However, there are still more works to explore the catalytic mechanism.

The coke formation on surface of catalyst is the main reason for the catalyst deactivation. As we know, iron species possess inherent anti-coking properties, and thus, they are wildly applied as a promoter to protect the catalyst against carbon deposits. For example, Michorczyk et al. [150] investigated the catalytic performance of Fe-based catalysts (e.g., pure Fe2O3, Fe2O3/AC, Fe2O3/MgO, and Fe2O3/γ-Al2O3) in the CO2-ODHP. They found that the reduced Fe2+ can be stabilized on alkaline supports of Al2O3 and MgO, which would be re-oxidized by CO2. Subsequently, Wang and Tsilomelekis [66] combined Fe with CeO2 to catalyze the CO2-ODHP and found that a high amount of Fe could minimize cracking. All the tested Fe-based catalysts exhibited comparable stability over 20 h continuously. However, the reduction in FeOx nanoparticles/clusters in supported Fe-based catalysts could be carbonated to FeC2 in light alkane dehydrogenation, which further catalyzed the coke formation, resulting in deactivation [151]. Thus, the stability of FeOx was the key for the reaction. Xiao et al. introduced Fe into the framework of MFI siliceous zeolite to avoid the deep reduction and carbonization of Fe species, which exhibited extremely high performances and superior coke resistance in a 200-h run [152]. Besides, the modified zinc cations in Zn-modified zeolites were similar to Ga species in Ga-modified zeolites. ZnO dissociated the adsorbed propane to form C3H6, which was strongly dependent on the relative position of [Zn-C3H7]+ and framework attached H+ [153]. Yue et al. reported that a high Si/Al ratio in a ZnO/HZSM-5 catalyst could decrease the Si/Al molar ratio to suppress the side reactions, such as cracking, oligomerization and aromatization [154]. The ZnO/HZSM-5(160) (160 is the Si/Al molar ratio) catalyst exhibited the best performances with a propane conversion of 41.5% and a propene yield of 25.8% at a steady state for the CO2-ODHP. Afterward, they treated HZSM-5 by steam to decrease the amount of Brønsted acid sites on the ZnO/HZSM-5 catalysts for suppressing coke formation. By this way, the catalyst offered a high propylene yield of 29.7% and possessed superior stability [155].

The catalytic performances of various Cr-free catalysts used in the CO2-ODHP reaction are collected in Table 2.

3 Roles of CO2 in CO2-ODHP reaction

For a long time, CO2 has been extensively studied because of its special advantages in the DHP. Under normal circumstances, for variable-valence metal catalysts such as Cr and V metals, the metal will be reduced to low valences by the reactant molecules, and CO2 as a weak oxidant can effectively recover these metals. By using CO2, the deep oxidation of propane can be avoided, and relatively high propylene selectivity can be ensured. In addition, CO2 can react with H2 generated from the DHP reaction to produce CO and H2O via the RWGS, promoting the dehydrogenation reaction to proceed and improving the activity of the catalyst. Besides, CO2 can react with the coke formed in the reaction to produce CO via the reverse Boudouard reaction and further avoid the catalyst deactivation, as well as effectively prolong the lifetime of a catalyst.

3.1 Promote redox cycle of redox-active metal oxides

In terms of redox metal catalysts (e.g., Cr-, V-, Ce-, and Mo-based catalysts), CO2 can be used as a soft oxidant to maintain the high valence state of the active sites at reaction atmosphere to benefit the dehydrogenation of propane to propylene and enhance the stability of catalysts [67, 83, 156]. It is generally believed that the redox metal catalysts follow the MvK mechanism in the CO2-ODHP reaction. The MOx species are simultaneously reduced to MOx−1 by propane to form propylene, and then, the reduced MOx−1 species are re-oxidized to MOx species by CO2 to form H2O. The redox cycle between MOx and MOx−1 under the promotion of CO2 plays an important role in the CO2-ODHP reaction over redox metal catalysts. For example, the Cr2O3 with coordinatively unsaturated Cr6+ in Cr-based catalysts is the active site in the DHP, which can be reduced to Cr3+ by propane and the reduced Cr3+ can be
simultaneously reoxidized to Cr$^{6+}$ by CO$_2$ [156–158]. Despite their high activities, the coke deposition and deep reduction of CrO$_{x-1}$ also lead to a rapid deactivation [159]. Fortunately, the introduction of promoters can improve this phenomenon. Yi et al. introduced Ni as a promoter into a CrO$_x$/SBA-15 catalyst for the CO$_2$-ODHP [160]. The ex-situ XPS results revealed that Cr$^{3+}$ was maintained only in the Ni-promoted catalyst, whereas Cr$^{3+}$ was easily reduced to Cr$^{2+}$ in the non-promoted catalyst during the reaction. The role of Ni in the catalyst elucidates that Ni induces the dissociation of CO$_2$ to CO and activated O (O$^{*}_{ads}$). Then, the generated O$^{*}_{ads}$ regenerates the reduced CrO$_x$ (Fig. 16). Recently, Liu et al. reported that the DHP and the CO$_2$-ODHP coexisted over Cr-based catalysts and further proved that the polymeric Cr$^{6+}$ oxides were more active but less selective than the isolated Cr$^{6+}$ oxides for the CO$_2$-ODHP, the amount of which was increased with the increasing degree of the polymerization for the polymeric Cr$^{6+}$ oxides [53]. And the polymeric Cr$^{6+}$ oxides with a high degree of polymerization were the high propane conversion but the least selective sites for the CO$_2$-ODHP.

**3.2 Promote RWGS reaction**

Even the RWGS reaction is thermodynamically limited, it is a way to proceed under the conditions of the PDH (500–600 °C), which can shift the equilibrium to produce more C$_2$H$_6$ [161–163]. Cao et al. demonstrated that the promotion of CO$_2$ on the yield of propylene was attributed to the promotion of simple dehydrogenation by coupling with the In-based catalysts for RWGS reaction [132, 133]. Through continuous H$_2$-CO$_2$ mixed gas pulse experiments, Liu et al. proved that the in situ generated H$_2$ in the reaction was also consumed by the RWGS reaction on the GaN-based catalyst, thereby improving the activity of the catalyst [47, 126]. Galvita et al. carried out the reaction in the feed of D$_2$/C$_3$H$_8$/CO$_2$ with a ratio of 1:1:1, only 45% of the resulting water-contained D$_2$O, confirming that the reaction followed both of the CO$_2$ oxidative dehydrogenation route and the RWGS in combination with the non-oxidative dehydrogenation route [83]. This broke the previous understanding that the two reaction pathways were mutually exclusive and provided a new idea for a clearer understanding of the reaction mechanism of the CO$_2$-ODHP.

**3.3 Promote reverse Boudouard reaction**

The coke deposition is the main reason for the deactivation of catalysts, which is composed of graphitized and amorphous carbons resulting from cracking, oligomerization, and aromatization of propylene [164]. Liu et al. compared the amount of coke deposition over a 5 wt% GaN/Q-3 catalyst after use in the dehydrogenation of propane with or without CO$_2$ [47]. They found that the catalyst possessed more amount of coke deposition in the absence of CO$_2$, indicating that CO$_2$ could effectively restrict the carbon deposition. In addition, Raman spectroscopy analysis revealed that a higher proportion of graphitic carbon was observed for the 5 wt% GaN/Q-3 catalyst used in the CO$_2$-ODHP, indicating that CO$_2$ could consume the amorphous carbon on surface of catalyst via reverse Boudouard reaction, resulting in the corresponding deposited coke with a higher graphitization degree.

**4 Summary and outlook**

In this review, the opportunities, catalyst development, mechanism, and role of CO$_2$ in the CO$_2$-ODHP have been summarized. CO$_2$-ODHP, as a potential alternative route to the DHP, not only has the potential to remedy the demand gap of propylene, but also can reduce the CO$_2$ concentration in the environment. CO$_2$ used as a soft oxidant can
avoid the over-oxidation of propane and propylene in the O\textsubscript{2}-ODHP. It has at least the following three functions: (1) CO\textsubscript{2} can maintain the high oxidation state of the catalytic active sites of some redox catalysts; (2) CO\textsubscript{2} can remove the in situ produced H\textsubscript{2} to value-added CO via the RWGS reaction; (3) CO\textsubscript{2} can also delay the formation of coke over the catalyst surface via the reverse Boudouard reaction to prolong the lifetime of a catalyst. To date, there are several catalytic systems such as redox-type metal oxide catalysts (Ce and V), main group metal oxide catalysts (Ga and In), and precious metal (Pt, Rh, Ru, and Pd) in the CO\textsubscript{2}-ODHP, igniting the hope of commercialization of this process. Despite these achievements, there are still lots of works to be done before the industrial application of the CO\textsubscript{2}-ODHP.

In terms of catalyst design, an efficient catalyst should possess the abilities of selective activation of C–H bond of propane and prohibition of C–C cleavage. It is also efficient for activation of C=O bonds of CO\textsubscript{2} to improve the yield of propylene and the efficiency of CO\textsubscript{2} utilization. One possible way is to construct some bifunctional catalytic systems, namely the catalytic active center is responsible for dehydrogenation and the support is responsible for activation of C=O bonds of CO\textsubscript{2}. Thus, it is critical to accurately identify the active sites and in-depth understand the interaction between the metal and the support. Besides, the competitive adsorptions among C\textsubscript{3}H\textsubscript{8}, C\textsubscript{3}H\textsubscript{6} and CO\textsubscript{2} cannot be ignored, which have influences on the propane conversion, propylene yield, and CO\textsubscript{2} utilization. That may be controlled via adjusting the texture structure and acid–base properties of catalyst.

Besides, the accurate establishment of the reaction mechanism for the CO\textsubscript{2}-ODHP can help to understand the reaction path, which in turn guides the design of catalyst. Thus, it is critical to capture the intermediates in the reaction. Fortunately, it has greatly facilitated the capture and analysis of reaction intermediates with the development of various in situ characterization techniques and theoretical calculations in recent years.

Then, the catalyst deactivation, resulting from coke deposition and sintering of active components on catalyst surface, seriously troubles the industrial application of catalysts. That may be avoided via optimizing reaction conditions such as temperature, partial pressure, and the type of reactor. In addition, it is also an effective method to introduce promoters into catalysts.

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Declarations

Conflict of interests The authors declare that they have no conflict of interest.

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