Abstract

CO₂ can be used as a soft oxidant for oxidative dehydrogenation of light alkanes (CO₂-ODH), which is beneficial to realize the reuse of CO₂ and meet the demand for olefins. The core of this reaction is the catalyst. Cr-based catalysts have attracted much attention for their excellent catalytic performance in CO₂-ODH reactions due to their various oxidation states and local electronic structures. In this paper, the synthesis and modification methods of Cr-based catalysts for CO₂-ODH are reviewed. The structure–activity relationship and reaction mechanism are also summarized. Moreover, the reasons for the deactivation of Cr-based catalysts are analysed and the main challenges faced by Cr-based catalysts in the CO₂-ODH process, as well as the future development trend and prospect, are discussed.

Keywords: Cr-based catalysts, CO₂, alkane, oxidative dehydrogenation, olefin
Introduction

Ethylene, propylene, butene and styrene are important raw materials for chemical production, which can be used for the synthesis of a series of polymers, such as polyvinyl chloride, polypropylene, polystyrene, etc. These products are widely applied in fields such as textiles, plastics, synthetic rubber and others [1, 2]. In recent years, the global demand for propylene has reached 90 million tons/annum (t/a), which is expected to further increase to 130 million tons by 2023, with an average annual growth rate of ~5% [3, 4]. With the rapid development of China, the production of olefins is increasing year by year. In 2020, the annual production of ethylene alone exceeded 20 million tons (Fig. 1) [5], almost double that of 2009. However, due to the rapid growth of demand in domestic and foreign markets, China still needs to import a large amount of olefins; for example, in 2019, China’s propylene imports exceeded 3 million tons [6].

The traditional methods for the industrial production of light olefins mainly include steam cracking and catalytic cracking. Steam cracking uses water and hydrocarbons such as ethane, propane or naphtha as raw materials, and is mainly used to produce ethylene with propylene and butadiene as the main by-products [7]. Alternatively, the major purpose of catalytic cracking is to produce light oil, while olefins are by-products [8]. However, disadvantages of the above two methods are obvious: on the one hand, both steam cracking and catalytic cracking need to be carried out under high temperature and high pressure, resulting in high equipment investment, and under such conditions, the used catalysts are prone to coking and deactivation [7]. Meanwhile, the products of the above processes are mixtures of multiple hydrocarbons and thus subsequent distillation-based separation is necessary to obtain targeted products, which considerably increases the energy consumption and CO₂ emission of the process.

In recent years, with the continuous development of horizontal wells, hydraulic fracturing and other technologies, production of unconventional natural gases such as shale gas has increased rapidly, in which a large number of low-carbon alkanes such as ethane and propane are produced. Therefore, the emerging process of olefin production by the dehydrogenation of alkanes has attracted extensive attention. This approach can potentially circumvent the problem of low product selectivity in traditional methods and milder reaction conditions are also a benefit for the stability of the catalysts. Dehydrogenation of alkanes includes direct dehydrogenation (DDH) and oxidative dehydrogenation (ODH). Currently, the DDH process has been industrialized. For example, the Catofin process uses a K(Na)–CrO₃/Al₂O₃ catalyst for the dehydrogenation of propane and isobutane at 560–650°C, and, in the Oleflex process, a Pt-based catalyst and a moving bed are used to convert propane into propene at 525–705°C and 1–3 bar, respectively [9, 10].

Although the reaction temperature of DDH is significantly lower than that of steam cracking and catalytic cracking, the process is still endothermic and needs to be performed at temperatures of >600°C in general. Moreover, there are also other issues related to DDH, such as coking, carbon deposition and the frequent regeneration of catalysts. Compared with DDH, ODH of alkanes using an external oxidant can not only promote the reaction balance to the product side, but also realize energy integration, reduce reaction temperature and catalyst coking, improve process stability and lower operation complexity.

The selection of oxidants is one of the key factors for ODH. As a widely used oxidant, oxygen can effectively reduce the reaction temperature and alleviate the coking on the catalyst surface. However, due to its strong oxidizing properties, deep oxidation of alkanes and the produced olefins can easily occur, leading to the formation of a large number of carbon oxides, which greatly reduces the selectivity of olefin products.

In recent years, employing CO₂ as a weak oxidant for the ODH of alkanes (CO₂-ODH) has gradually become one of the research focuses in the field of energy and the chemical industry. This process has several advantages: (i) CO₂ is a relatively weak oxidant, which can effectively avoid the deep oxidation of alkanes and their dehydrogenation products; (ii) CO₂ can react with the H₂ produced by dehydrogenation via the reverse water–gas shift reaction, which shifts the dehydrogenation reaction balance to the product side and thus improves the conversion of alkanes; (iii) under the CO₂-ODH reaction condition, CO₂ can also react with the carbon species deposited on the surface of the catalyst by the Boudouard reaction (CO₂ + C = 2CO), so as to improve the stability of the catalyst; (iv) the CO₂-ODH process uses hydrogen produced by the dehydrogenation reaction to convert CO₂ into CO, which offers a potential option for the utilization and emission reduction of CO₂, and may play a role for the realization of the goal of carbon neutrality in the future.

In the past two decades, a series of CO₂-ODH catalysts has been developed. Mo, Zn, Mn, Co, V, Ga and Cr are the most frequently used active components for CO₂-ODH. Koirala et al. studied the CO₂-ODH reaction of ethane catalysed by CoOₓ/SiO₂. The activity test results showed that ethylene production first increased and then decreased with the increase in cobalt loading [11]. Kainthla et al. prepared a MoO₃/TiO₂–Al₂O₃ catalyst by impregnation, which can be used to catalyse the CO₂-ODH reaction of ethylbenzene [12]. Gomez et al. prepared a series of catalysts with bimetallic active centres (Pt, Pd, Ni, Co, Fe mixed in pairs) and loaded them onto CeO₂. It was found that a Fe₃Ni₁/ CeO₂ catalyst had the best propene selectivity among all the catalysts. When the Ni content increased further, propene selectivity decreased and the reaction was in favour of a dry reforming reaction [13]. Wang et al. found that a GaN/NaZSM-5 catalyst showed high propylene selectivity because of the appropriate tuning of the acid/basic properties of the support [14]. However, the performance of non-chromium catalysts is generally inferior to that of Cr-based catalysts, and Cr-based catalysts are the most
widely studied systems due to the following advantages: (i) high catalytic activity, (ii) low price and (iii) relatively high stability. In recent years, several excellent reviews related to CO$_2$-ODH have been published. However, most of them mainly paid more attention to the available catalysts for different alkanes. Therefore, this paper reviews and summarizes the research progress on Cr-based catalysts for CO$_2$-ODH. We pay special attention to the methods of preparation, structural–performance relationship, reaction mechanism and catalyst deactivation. Furthermore, a future perspective is also presented.

1 Preparation of a Cr-based catalyst for CO$_2$-ODH

Because Cr$_2$O$_3$ can catalyse the direct dehydrogenation of alkanes, the performance of pure Cr$_2$O$_3$ for CO$_2$-ODH was investigated in early work. The results showed that the conversion of alkanes and the selectivity for olefins were low [15, 16], which may be related to the low dispersion state of Cr$_2$O$_3$. Therefore, a dispersed Cr-based catalyst has been the main direction over the past two decades.

Table 1 shows the catalytic performance of some dispersed Cr-based catalysts.

1.1 Impregnation-derived Cr-based catalysts

Impregnation is the most widely used preparation method of Cr-based CO$_2$-ODH catalysts. Ge et al. prepared Cr-based catalysts by impregnation using Al$_2$O$_3$, TiO$_2$, MCM-41 and ZrO$_2$ as supports, and their catalytic performance for CO$_2$-ODH was found to be significantly better than that of pure Cr$_2$O$_3$ [16]. Kocoń et al. studied the performance of Cr$_2$O$_3$ supported on Al$_2$O$_3$ and SiO$_2$ for the CO$_2$-ODH reaction; they found that, compared with the direct dehydrogenation, the conversion of propane on CrO$_x$/SiO$_2$ was improved in the presence of CO$_2$, while the presence of CO$_2$ was detrimental to the conversion of propane on CrO$_x$/Al$_2$O$_3$ [17]. Similar results were also reported from Shishido and co-workers. By comparing the effects of different CO$_2$ concentrations on Cr/SiO$_2$ and Cr/Al$_2$O$_3$ for the CO$_2$-ODH reaction, they found that the adsorption of CO$_2$ on Al$_2$O$_3$ was too strong, which inhibited the adsorption of propane, resulting in an adverse effect on the activation and conversion of propane [18]. Wang et al. prepared a series of Cr$_2$O$_3$ catalysts supported on oxide supports. They found that the type of support had a significant effect on the surface acidity and basicity of the final catalyst, the phase state of the Cr$_2$O$_3$ and its dispersion. Thus, performance of the catalysts in CO$_2$-ODH can be regulated. At 650°C and 1 bar, the activity of the catalysts decreased in the order of Cr$_2$O$_3$/SiO$_2$ > Cr$_2$O$_3$/ZrO$_2$ > Cr$_2$O$_3$/Al$_2$O$_3$ > Cr$_2$O$_3$/TiO$_2$ [19]. In particular, although some work has pointed out that the competitive adsorption of CO$_2$ and alkanes has a negative impact on the activation and conversion of alkanes, this phenomenon is often only related to the conversion rate at the initial stage of the reaction. With the progress of the reaction, serious carbon deposition during DDH will lead to rapid deactivation and thus the positive effect of CO$_2$ on the stability of the catalyst will be gradually dominant [20].

For the preparation of a Cr-based CO$_2$-ODH catalyst by the impregnation method, SiO$_2$ is the most widely used support, which is related to its flexible porosity and morphology. For example, by comparing the performance of SBA-15, ZrO$_2$ and Al$_2$O$_3$ as the supports, Zhang et al. found that the activity, selectivity and stability of Cr$_2$O$_3$/SBA-15 were better than those of the other two supports. The author
proposed that this was mainly due to the weak interaction between CrO₃ and SBA-15, which affected the existing form of Cr species and weakened the trend for deep dehydrogenation of alkanes. Therefore, the selectivity of the reaction was improved and the formation of carbon on the surface of the catalyst was alleviated [21].

Until now, the use of amorphous porous SiO₂, various kinds of silica-based molecular sieves and ordered mesoporous SiO₂ as supports for Cr-based CO₂-ODH catalysts has been widely reported. Botavina and co-workers introduced CrOₓ on commercial SiO₂ by the impregnation method. By optimizing the loading amount of Cr, the Cr species on the catalyst and its dispersion can be adjusted, so as to obtain a CO₂-ODH catalyst with catalytic performance meeting industrial requirements [22]. Zhao et al. used a TS-1 molecular sieve as the support, then Cr₂O₃ was introduced by impregnation and its performance in the CO₂-ODH reaction was studied. The results showed that when the Si/Ti ratio was 30, the ethane conversion reached 47.4% at 650 °C with an ethylene selectivity of 90.0% [23]. A mesoporous silica (MSU-x) molecular sieve was employed by Liu et al. as a carrier, where different amounts of CrOₓ were introduced, and the obtained catalysts showed excellent CO₂-ODH performance. At 873 K, a propane conversion of 50.4% and a propene yield of 42.1% were achieved, respectively [24]. Other molecule sieves, such as ZSM-5, were also used as a catalyst support for the preparation of Cr-based CO₂-ODH by the impregnation method and varying performance was reported [25, 26]. As an important family of porous SiO₂, ordered mesoporous SiO₂ was widely used for catalysis. Michorczyk et al. found that due to the ordered porosity and higher surface area, CrOₓ species could be better dispersed on the surface of SBA-1 and SBA-15 compared to that on amorphous SiO₂, and thus their performance for CO₂-ODH was better [27]. Michorczyk et al. prepared a CrOₓ/MCM-41 catalyst and systematically investigated the effects of Cr loading and reaction temperature on the performance in the propane CO₂-ODH reaction. On the optimum catalyst (Cr6.8/MCM-41), the propylene selectivity was >80% and the conversion of propane increased from 21% at 772 K to 62% at 923 K [28]. Asghari et al. studied the

| Catalyst                  | T/°C | Propane/ethane | Alkane conversion/% | Olefin selectivity/% | V(CO₂)/V(alkane) | Reference |
|---------------------------|------|----------------|---------------------|---------------------|-----------------|-----------|
| Cr₂O₃/SiO₂-A (0.97 wt%)   | 600  | P              | 16.2                | 91.3                | 5.0             | [15]      |
| 5%Cr/ZrO₂                 | 650  | P              | 46.5                | 76.1                | 3.6             | [16]      |
| (3.4)CrOₓ/Al₂O₃           | /    | P              | 29.7                | 80.5                | 7.0             | [17]      |
| Cr/SiO₂                   | 550  | P              | /                   | /                   | 1.7             | [18]      |
| 5 wt% Cr₂O₃/SiO₂          | 650  | E              | 56.1                | 92.9                | 5.0             | [19]      |
| Cr₂O₃-ZrO₂-180            | 550  | P              | 53.3                | 79.0                | 2.0             | [20]      |
| Cr₂O₃ (2)/SBA-15          | 550  | P              | 24.2                | 89.3                | 2.0             | [21]      |
| 5%Cr/SiO₂                 | 600  | P              | 47.0                | 87.0                | 2.0             | [22]      |
| Cr/TS-1(150)              | 650  | E              | 62.2                | 81.0                | 4.0             | [23]      |
| 12%Cr/MSU-x               | 600  | P              | 54.5                | 84.2                | 3.0             | [24]      |
| 3Cr/NaZSM-5-160           | 650  | E              | 61.3                | 78.9                | 5.0             | [26]      |
| Crₓ/SBA-1                 | 550  | P              | 33.2                | 87.9                | 5.0             | [27]      |
| Crₓ/MCM-41                | 550  | P              | 40.0                | 88.0                | 5.0             | [28]      |
| Cr(8%)/MCM-41             | 700  | E              | 35.0                | 94.0                | 5.0             | [29]      |
| SrCr/SiOₓ#Hₓ               | 700  | E              | 31.7                | 79.8                | 1.0             | [30]      |
| Cr(8)/MOS                 | 700  | E              | 50.4                | 90.1                | 5.0             | [31]      |
| Cr(5%)/ZrO₂               | 700  | E              | 48.0                | 91.0                | 5.0             | [32]      |
| 7%Cr/MMS-2                | 600  | P              | 38.0                | 88.0                | 4.0             | [33]      |
| Cr-MSU-x28                | 600  | P              | 25.0                | 93.0                | 1.0             | [34]      |
| 5 wt% Cr-TUD-1            | 650  | P              | 45.0                | 75.0                | 0.2             | [35]      |
| 0.04Cr/SBA-1              | 650  | P              | 55.2                | 76.7                | 5.0             | [36]      |
| 7Cr/ZrO₂                  | 550  | P              | 63.0                | 63.0                | 2.0             | [37]      |
| 8 wt% Cr/MCM-41-Cr-TEOS   | 700  | E              | 59.0                | 75.0                | 5.0             | [38]      |
| ZrCr/SiO₂                 | 700  | E              | 38.3                | 72.1                | /               | [39]      |
| Cr/ZSM5-ZrO₂(10)          | 700  | E              | 64.0                | 88.0                | 5.0             | [40]      |
| Cr/Te-MCM-41(Si/Te=50)-p  | 700  | E              | 64.0                | 97.0                | 5.0             | [41]      |
| Cr/ZSM5–CeO₂(10)          | 700  | E              | 71.0                | 87.0                | 5.0             | [42]      |
| Cr(8)/Ti(1.9)/MCM-41      | 700  | E              | 45.0                | 94.0                | 5.0             | [43]      |
| Ru,Cr₂O₃/SiO₂             | 496  | P              | 8.0                 | 88.0                | 1.0             | [44]      |
| CrOₓ/Al₂O₃                | 700  | E              | 20.0                | 90.0                | 2.0             | [45]      |
| Cr/ZSM-5-5-0.4            | 650  | E              | 65.5                | 75.4                | 5.0             | [51]      |
| Cr/MCM-41                 | 550  | P              | 15.0                | 88.0                | 5.6             | [53]      |
| 0.5 Ni-Cr/Si               | 600  | P              | 24.0                | 88.0                | 1.0             | [54]      |
| 0.5%CrOₓ/silicalite-1      | 650  | E              | 36.4                | 94.0                | 5.0             | [55]      |
performance of a CrOx/MCM-41 catalyst for the ethane CO2-ODH reaction. They found that the loading of Cr changed the catalytic performance through the influence on particle size, Cr dispersion, specific surface area and other physical and chemical properties [29]. Li et al. prepared a SrCr/SiO2 catalyst with better performance by combining the impregnation method with plasma treatment. The initial conversion rate of ethane reached 78.1% after the catalyst was treated with plasma in an H2 atmosphere. It was found that the dispersion of the metal and the number of oxygen vacancies increased after plasma treatment. According to the possible reaction mechanism (Fig. 2), these factors are beneficial to improving the activity of the catalyst [30]. Abdulrhman et al. used an impregnation method to load elemental Cr onto a mesoporous organosilica (MOS) carrier to obtain a Cr/MOS catalyst. The ethane conversion and ethylene selectivity of Cr(8)/MOS reached 50.4% and 90.1%, respectively. The high performance was attributed to the presence of a reducible Cr (VI) species on the catalyst surface [31].

1.2 One-pot synthesis of Cr-based catalysts

In addition to impregnation, Cr-based catalysts were also prepared using a one-pot method. Talati prepared Cr/ZrO2 and Cr/TiO2 catalysts by the impregnation method and co-precipitation method, respectively. The results showed that higher specific surface areas were obtained for the co-precipitated samples, which facilitated the dispersion of Cr species. Therefore, higher performance for CO2-ODH could be obtained [32]. Wang and co-workers established that, during the one-pot preparation of mesoporous SiO2 nanospheres that supported CrOx catalysts, the sequence of precursor addition had a profound influence on the performance of the final catalyst. When the Si and Cr source were added at the same time into the micelle system composed of a mixed solution of cetyltrimethyl ammonium bromide and triethanolamine (TEAH3), the performance of the obtained Cr/MSS-2 catalyst was the best, which was mainly related to the better CrOx dispersion and acidic sites of appropriate strength on the catalyst [33]. Baek et al. also reported that the one-pot method was beneficial to improving the dispersion of active CrOx sites, so the performance of the obtained Cr-MSU-x system in the CO2-ODH of propane was better than the impregnation-derived Cr/MSU-x catalyst [34]. Burri et al. reported rapid preparation of a Cr-TUD-1 catalyst by the one-pot method under microwave irradiation. This method realized the coating of Cr sites in the channels of TUD-1 (Technische Universiteit Delft), a 3D mesoporous network structure, and excellent specific surface areas of >600 m2/g were obtained. As a result, the propane conversion reached 45% at 550°C and the selectivity for propylene exceeded 75% [35]. Oliveira et al. synthesized Cr/ZrO2 catalysts using the conventional hydrothermal method and the microwave hydrothermal method, respectively. The results showed that the samples prepared using the microwave method had smaller particle size and their catalytic performance in CO2-ODH was higher than those prepared by the conventional hydrothermal method. It should be pointed out that, independently of the used hydrothermal conditions, the strong adsorption between CO2 and ZrO2 will adversely affect the adsorption activation of alkanes. Therefore, the initial conversion of alkanes in the direct dehydrogenation process is higher than that in the oxidative dehydrogenation process of CO2. However, because the presence of CO2 is beneficial to the removal of carbon species on the catalyst surface, the CO2-ODH process is more stable. With the progress of the reaction, the conversion of alkanes under CO2-ODH conditions gradually exceeds that of the direct dehydrogenation process [1]. Wu et al. prepared CrOx-ZrO2 catalysts via a co-precipitation method from zirconium oxynitrate and chromium nitrate, and investigated the effect of hydrothermal treatment on the performance of the catalyst. The results showed that additional hydrothermal treatment
could increase the Cr(VI) content in the final catalyst, resulting in improved CO₂-ODH performance. The hydrothermal temperature was also optimized to be 180°C and an initial conversion of propane reached 53.3% [20]. Michorczyk et al. prepared a Cr-SBA-1 catalyst using a one-pot method and studied the effects of Cr content and reaction conditions on the catalytic performance of propane CO₂-ODH. With the optimized catalyst, conversion of propane reached 55.2% and the selectivity for propylene was 76.7% at 650°C [36]. Xie et al. prepared CrOₓ-ZrO₂ catalysts with different CrOₓ content using the evaporation-induced self-assembly method. Due to the templating effect of P123 surfactant, the catalyst had a remarkably improved self-assembly method. Due to the templating effect of P123 surfactant, the catalyst had a unique wormlike mesoporous structure. The Cr(VI) species distribution on 7Cr-ZrO₂ was the most favourable for the catalytic performance of CO₂-ODH. At 550°C, the initial conversion of propane was 68.0% and the selectivity for propylene was 40.5%. Besides, the deactivation rate was the slowest [37]. Abdulrahman and his team reported the one-pot synthesis of a Cr-MCM-41 catalyst. The catalyst had high specific surface area and pore volume, which facilitated the diffusion of reactants to the active Cr sites, and the higher the Cr(VI)/Cr(III) ratio, the better the activity of the catalyst [38].

1.3 Modification of Cr-based catalysts
Performance of Cr-based catalysts for CO₂-ODH can be promoted by modification of either the support or the Cr sites. Li et al. modified Cr/SiO₂ catalysts by Zr, Ce, Sr and Sn, and reaction evaluation showed that Zr and Ce were beneficial to the conversion of ethane, while the modification of Sr and Sn would reduce the catalytic performance. The researchers believed that this was mainly due to the influence of different promoters on the reversibility of the oxidation-reduction process of Cr species on the catalyst surface [39]. Haghighi and co-workers prepared ZrO₂-modified ZSM-5 and CeO₂-modified MCM-41 as the supports to prepare Cr-based catalysts. It was shown that the introduction of a certain amount of modifier could significantly improve the dispersion state of Cr species, which was responsible for the improvement of CO₂-ODH performance [40, 41]. Rahmani et al. introduced CeO₂ particles during the preparation of ZSM-5 and they found that a certain amount of CeO₂ modification could effectively improve the dispersion and reducibility of Cr sites, thus contributing to the improvement of CO₂-ODH performance [42]. By using a second-deposition procedure, MCM-41 was modified by TiO₂ by Al-Awadi and the results of XRD, TEM and SEM showed that the presence of TiO₂ changed the dispersion of Cr species, particle size and the interaction between the Cr and the support, which significantly affected the reaction performance of the catalyst. At 700°C, the conversion of ethane and selectivity for ethene reached 51.87% and 80%, respectively [43]. Jin and his team modified the Cr/SiO₂ catalyst by adding elemental Ru. It was found that the conversion rate of propane increased gradually when the content of Ru was <1 wt%. Compared with the Cr/SiO₂ catalyst without Ru, the propylene production rate of 1 wt% Ru–Cr/SiO₂ catalyst increased by 100%. The reason is that Ru can promote the activation of propane and carbon dioxide. However, the presence of excessive Ru will adsorb more carbon dioxide and promote dry reforming of propylene, leading to decreased selectivity of propene (Fig. 3) [44].

2 Structure–performance relationship and reaction mechanism
In addition to the general factors such as the specific surface area and surface abundance of active sites, other parameters that may significantly affect the performance of Cr-based catalysts for CO₂-ODH mainly include the oxidation state and coordination of chromium and the redox property of the Cr species, the acidity and basicity of the catalysts, etc. For example, Bugrova et al. systematically studied the CO₂-ODH performance and reaction path of supported CrOₓ towards the CO₂-ODH of ethane. It was found that CrOₓ/γ-Al₂O₃ and CrOₓ/ZrO₂ had the highest ethylene-formation rate, but their reaction paths were significantly different: the Cr species on CrOₓ/γ-Al₂O₃ would be irreversibly reduced, so ethylene was mainly formed by direct dehydrogenation of ethane, while CO₂ and H₂ reacted via the reverse water–gas shift. At the same time, due to the strong surface acidity of the catalyst, carbon deposition was accelerated via ethane cracking, resulting in the deactivation of the catalyst. For CrOₓ/ZrO₂ on the other hand, the Cr sites with high valence state were relatively stable and their reducibility was poor. These sites were more effective for CO₂ to participate in the dehydrogenation process of ethane. At the same time, the weak acidity of the catalyst also helped to avoid the formation of a large amount of carbon deposition and sintering was the major reason for the deactivation of the catalyst [45].

2.1 Redox property of the Cr species
The redox behaviour of Cr species is one of the decisive factors for the catalytic performance in CO₂-ODH. At present, most research has demonstrated that Cr exists in a hexavalent state after preparation, which has high performance of the dehydrogenation of alkanes. However, Cr(VI) will be reduced to less active Cr(III) during the activation of alkanes. In the process of the direct dehydrogenation of alkanes, this reduction is often irreversible, resulting in the deactivation of the catalyst. In the process of CO₂-ODH, Cr(III) is expected to be reoxidized to Cr(VI) by CO₂, so that the catalyst remains active. In other words, the CO₂-ODH process is closely related to the redox cycle of Cr species during the reaction [46–50]. For example, Li et al. found that on Cr/SiO₂ catalyst, ethane molecules were first adsorbed on the Cr(VI) sites and then oxidized by lattice oxygen. In the process, Cr(VI) was reduced to Cr(III) and...
lattice oxygen was converted to hydroxyl oxygen, resulting in the formation of oxygen defects on the surface of the catalyst. Subsequently, Cr(III) was reoxidized to Cr(VI) by CO$_2$ and the lattice oxygen was recovered, thus forming a closed cycle of catalytic process. In the above process, the abundance of lattice oxygen on the catalyst surface and whether Cr(III) can be reoxidized are the key factors in determining the performance of the catalyst, which is closely related to the selection of promoters (Fig. 4) [39]. Similarly, Wu et al. performed XPS measurement and showed that most of the Cr(IV) on the surface of the Cr$_2$O$_3$–ZrO$_2$ catalyst was reduced to Cr(III) in both the CO$_2$-ODH reaction and the DDH of alkanes without CO$_2$. However, after the CO$_2$-ODH reaction, the Cr(VI)/Cr(III) ratio on the surface of the catalyst was significantly higher than that in the direct dehydrogenation, indicating that there was a redox cycle between Cr(VI) and Cr(III) in the process of the CO$_2$-ODH reaction [20]. Differently from the above reports, Xie et al. used in situ Raman spectroscopy to study the catalytic mechanism of the CO$_2$-ODH of propane on the Cr$_2$O$_3$–ZrO$_2$ catalyst. The results showed that, except for the induction period, Cr(VI) could not be detected on the catalyst and the real active site was the Cr(III) site derived from the reduction of 'polymeric Cr(VI)' species bearing both Cr–O–Cr and Cr=O bonding structures [37].

The close correlation between the redox property and the oxidation state and coordination of Cr species was also reported by Baek et al. In their work, two kinds of Cr species, namely ‘isolated Cr’ and ‘polymeric Cr’, were identified. It was found that their interaction with the support varied significantly due to the structural difference. Therefore, they could be furthered divided into soft Cr (weak interaction) and hard Cr (strong interaction). Soft Cr was easier to be reduced to Cr(III) and the Cr(III) was easier to be reoxidized to Cr(VI). Since the CO$_2$-ODH reaction is based on the cycling of Cr(VI) and Cr(III), the proportion of soft Cr in the catalyst is directly related to its performance (Fig. 5) [34]. Cheng et al. prepared a series of Cr/ZSM-5 catalysts.

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**Fig. 3:** Proposed catalytic pathways over different catalysts for an oxidative dehydrogenation of propane reaction. Reproduced from [44] with permission from the Royal Society of Chemistry.

**Fig. 4:** Possible reaction route of ethane dehydrogenation with CO$_2$ on promoted Cr/SiO$_2$ catalysts. Reprinted from [39]. Copyright 2019 American Chemical Society.
using ZSM-5 with different particle sizes as supports. The results showed that the number and type of silanol groups on the surface of various supports affected the dispersion state of Cr(VI) on the final catalyst surface, which regulated the number and distribution of reducible Cr sites, and further determined the performance of the catalysts [51].

2.2 Acid/basic properties

The surface acidity and basicity of the catalysts have a significant effect on the performance of Cr-based CO₂-ODH catalysts and both appropriate acidity and basicity are required for the reaction.

The basicity of the catalysts mainly affects the CO₂-adsorption behaviour of the catalysts. In most CO₂-conversion reactions, it is considered that stronger CO₂ adsorption is beneficial. However, for the CO₂-ODH process, strong CO₂ adsorption on the catalysts often affects the adsorption and activation of alkanes, lowering the conversion rate of the CO₂-ODH reaction. This is also the main reason for the observation that the introduction of CO₂ has an adverse effect on the dehydrogenation process of alkanes [1, 18]. In addition to affecting the competitive adsorption capacity of CO₂, the enhanced basicity of the catalysts also significantly weakens the catalytic activity of acidic sites to activate C–H bonds, thus affecting the activation of alkanes in the process of CO₂-ODH. For example, Ge et al. used K to modify a Cr₂O₃/SiO₂ catalyst and found that the conversion of propane was significantly reduced [16]. Similarly, Lapidus et al. also found that the introduction of Li and Na could replace the silanol H on the surface of a Cr₂O₃/SiO₂ catalyst, thus greatly reducing the activity of the catalyst [52].

The acidity of Cr-based catalysts is very important for their ability to activate alkanes. For example, Wang et al. reported the correlation between the activity of the CO₂-ODH reaction and the surface acidity of catalysts, and they established that moderate acid strength was key to ensuring the appropriate activation of alkanes: weak acidity cannot activate the C–H bond of alkanes, while acidity that is too strong will lead to the activation of multiple C–H bonds and the formation of a large amount of carbon deposition, which is adverse to the stability of the catalyst [33]. Rahmani et al. also reported that CeO₂ modification can reduce the surface acidity of ZSM-5, thus inhibiting the carbon deposition of the catalyst in the CO₂-ODH process and improving the stability [42]. Michorczyk et al. prepared a β-zeolite-supported Cr catalyst and the sample was dealuminated by acid washing. The results showed that the acid sites on the dealuminated catalyst were greatly reduced, which inhibited the strong adsorption of CO₂ and the direct dehydrogenation of propane, thus the activity and selectivity for CO₂-ODH were promoted [4].

3 Deactivation of catalysts

Carbon deposition is an important approach for the deactivation of catalysts in the dehydrogenation of various alkanes. The reason is that the C–C bond may break at high temperature, which leads to the cracking of alkanes and eventually forms various carbon-deposition species. The various carbon-deposition species deactivate catalysts by covering the active...
sites or blocking the pores. The behaviour of carbon deposition on Cr-based CO2-ODH catalysts is mainly related to the acidity of the catalysts, especially on the strongly acidic surface. Therefore, controlling the acidity is an important way to reduce the formation of inactive carbon-deposition species. Apart from the above mechanism, carbon-deposition species may be generated from different reaction pathways. For example, Xie et al. found that when the atmosphere was changed from 4% CO2/2% H2/Ar to 5% H2/Ar, new Raman absorption peaks appeared at 1395 and 1595/cm, which corresponded to the D-band and G-band absorption of the carbon species, respectively. Based on the above phenomenon, a new mechanism of carbon deposition was proposed. First, some Cr(III) sites appeared on the catalyst surface in hydrogen-rich environment, which could activate H2 and convert the adsorbed CO2 into carbon-deposition species [37].

In addition to carbon deposition, the irreversible reduction of CrOx can block the redox cycle of Cr species in the CO2-ODH reaction, resulting in the deactivation of Cr-based catalysts. Baek characterized the used Cr-MSU-x catalyst. The results showed that the amount of carbon deposited on the catalyst was very small, far from the amount that may affect the performance of the catalyst. However, after deep reduction, the performance of the catalyst decreased significantly. Furthermore, the author found that the treatment at 650°C in air could completely regenerate the deactivated catalyst and the catalyst performance remained stable in multiple cycles [34]. Takehira et al. also found that the oxidizing ability of CO2 was not enough to maintain the oxidation state of Cr species in a Cr-MCM-41 catalyst, which was the main reason for the gradual deactivation of the catalyst [53]. Yun et al. modified CrOx/SBA-15 with Ni using the consecutive impregnation method. The results showed that the unmodified CrOx/SBA-15 catalyst would be deactivated due to the reduction of Cr(III) to Cr(II) during the CO2-ODH of propane, while CO2 could be decomposed into CO with the formation of adsorbed active oxygen species on the Ni site, and the latter could further realize the reduction of reduced Cr species, so as to improve the stability of the catalyst (Scheme 1) [54]. Cheng et al. compared the stability of Cr/silicalite-1 and Cr/SBA-15 catalysts. After 6 h of reaction, the activity of Cr/silicalite-1 decreased by 9.8%, while that of Cr/SBA-15 decreased by 58%. The reason may be because the interaction between the CrOx and silicalite-1 surface was stronger, and the CrOx in the reaction process was less able to agglomerate, which could keep the activity of the catalyst unchanged [55].

### 4 Conclusions

On the whole, CO2-ODH is of great significance to the utilization of CO2 and to fill the demand gap for light alkenes, which has a broad development prospect. At present, the Cr-based catalyst is the most widely investigated and the most likely to be the first to achieve commercial application. The synthesis methods of Cr-based catalysts mainly include impregnation and the one-pot method. In addition, modification with different kinds of promoters can improve the activity and stability of the catalysts. At present, the mechanism of Cr-based catalysts has been studied in depth. The catalytic activity is closely related to the number of lattice oxygens and acid–base sites on the surface of catalysts. Although most of the current Cr-based catalysts have excellent performance, they still have the following problems: (i) although the stability of the Cr-based catalysts is higher than that of other active elements, it is still far from the requirement of industrial application; (ii) the high toxicity and environmental hostility of Cr may greatly hinder its commercial implementation. In order to solve these problems, future research may focus on: (i) in most of the present work, traditional preparation methods were used for the Cr-based catalysts, so new strategies such as atomic deposition, the utilization of framework materials as precursors and others should be explored; (ii) new supports including 2D materials and quantum dots may be used as they can provide interesting dispersion properties for the Cr species; and (iii) advanced characterization methods, such as X-ray absorption, in situ TEM may be used for the study of the structure–performance relationship, which may serve as a basis for the catalyst design.

### Conflict of interest statement

None declared.

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