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State-of-the-art catalysts for direct dehydrogenation of propane to propylene

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ABSTRACT

With growing demand for propylene and increasing production of propane from shale gas, the technologies of propylene production, including direct dehydrogenation and oxidative dehydrogenation of propane, have drawn great attention in recent years. In particular, direct dehydrogenation of propane to propylene is regarded as one of the most promising methods of propylene production because it is an on-purpose technique that exclusively yields propylene instead of a mixture of products. In this critical review, we provide the current investigations on the heterogeneous catalysts (such as Pt, CrO_x, VO_x, GaO_x-based catalysts, and nanocarbons) used in the direct dehydrogenation of propane to propylene. A detailed comparison and discussion of the active sites, catalytic mechanisms, influencing factors (such as the structures, dispersions, and reducibilities of the catalysts and promoters), and supports for different types of catalysts is presented. Furthermore, rational designs and preparation of high-performance catalysts for propane dehydrogenation are proposed and discussed.

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1. Introduction

Propylene is one of the most important raw materials for the production of many industrial products such as acrolein, polypropylene, acetone, polyacrylonitrile, and propylene oxide [1–8]. The traditional industrial processes for propylene production are fluid catalytic cracking and steam cracking of naphtha and light diesels [1,4]. With the rapid consumption of fossil-based energy, the traditional methods of propylene production cannot satisfy the growing demand for propylene. The development of an efficient and economic method of propylene

production is therefore of great importance, though challenging. Over the last several years, considerable efforts have been made to develop new efficient methods for propylene production, such as propane dehydrogenation (PDH) [1–8], methanol-to-olefins [9,10], and Fischer-Tropsch-to-olefins [11–13]. Among these methods, the PDH technique has been regarded as one of the most promising methods of propylene production, because it is an on-purpose method that exclusively yields propylene, instead of a mixture of products.

Furthermore, with the development of fracking technology, a large amount of shale gas can be extracted by this

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cost-effective method; propane is a main constituent of shale gas. The price of propane has decreased obviously, which provides a great opportunity for on-purpose catalytic dehydrogenation of propane to propylene [1,14–16]. Over the last several years, a number of reviews have summarized the oxidative dehydrogenation of alkanes to olefins by using nanocarbons, boron nitride, metals, and metal oxides [2,4,8,14–16]. However, direct dehydrogenation of alkanes to olefins is rarely reported [1,3,17]. Particularly, elaborate discussions and comparisons of the origins of the catalytic activities, reaction mechanisms, and functional adjustments of direct PDH catalysts are scarce.

In this work, the state-of-the-art catalysts that have been reported in recent years for direct dehydrogenation of propane to propylene are reviewed. The correlations between the properties and performances of the catalysts are discussed and summarized. Furthermore, the active sites, structural properties, and catalytic mechanisms of Pt, CrO_x, VO_x, GaO_x-based catalysts, and nanocarbons in direct PDH are analyzed and outlined. The influences of the preparation methods of the catalysts and the types of supports and promoters are highlighted.

2. Overview of direct PDH

Direct PDH is a thermodynamically limited highly endothermic process, as observed below [1,3,17].

It is notable that the C–H bonds of propane are highly stable, therefore, a high reaction temperature is required to realize C–H bond cleavage. Usually, a high temperature of ~550–700 °C is needed to achieve a high propane conversion [18–22]. Owing to the absence of oxidizing agents, the propylene selectivity in direct PDH is much higher than that in oxidative dehydrogenation reaction. To date, the direct PDH reaction has been used in industry, such as Catofin (Lummus, CrO_x-based catalysts) and Oleflex (UOP, Pt-based catalysts) technologies [21,23].

In direct PDH process, activation of the C–H bonds of propane is the most important step that determines the catalytic

performance of PDH catalysts. However, the product propylene molecules are more active than propane molecules. Side reactions, including cracking, deep dehydrogenation, and/or polymerization, occur during the PDH process, which result in low selectivity and coke formation [1,5,8,24–27]. Therefore, a good PDH catalyst must favor C–H cleavage over C–C cleavage. In the past several decades, a number of heterogeneous catalysts (such as Pt, CrO_x, VO_x, GaO_x-based catalysts, and nanocarbons) have been exploited for direct PDH reaction that have exhibited high performances. However, there are still some issues with these catalysts, such as low stability, serious coke formation, high prices, and environmental problems.

3. Direct PDH catalysts

3.1. CrO_x-based catalysts

Supported CrO_x are one of the most efficient catalysts for alkane dehydrogenation that have been studied for several decades [17,28–37]. Owing to the low price and high catalytic activity, CrO_x-based catalysts have been commercially utilized in Catofin craft [21,23,24]. Table 1 lists the recent reports on CrO_x-based catalysts for PDH reaction.

On fresh CrO_x-based catalysts, there are many kinds of Cr species, including Cr⁶⁺, Cr⁵⁺, Cr³⁺, Cr²⁺, isolated Crⁿ⁺, oligomeric Crⁿ⁺, and crystallite Cr₂O₃, which play different roles in the PDH process [30–32]. Rather difficultly, the Cr⁶⁺ species would be transformed into Cr³⁺ and/or Cr²⁺ during the PDH process due to the presence of H₂ [30,32]. Furthermore, the types of supports, Cr loading amounts, and preparation methods can have great influences on the types of Cr species present, and thereby, affect the catalytic performances of CrO_x-based catalysts [31,33–35]. It is reported that the Cr species supported on mesoporous silica SBA-15 are isolated Cr⁶⁺ at low Cr loadings (≤1%), which tend to aggregate into crystalline Cr₂O₃ particles as the Cr loading increases up to 5% [31]. When the Cr species are loaded on Al₂O₃, a fraction of the isolated and oligomeric Cr⁶⁺ species would be present in the Cr/Al₂O₃ catalysts. How-

Table 1

Summary of the catalytic data of CrO_x-based catalysts for PDH.

Catalyst	Reaction temperature (°C)	Flow rate (mL/min)	Space velocity ^a (h ⁻¹)	Feed composition	Conversion ^b (%)	Selectivity (%)	Space time yield ^c (h ⁻¹)	Catalyst life ^d (h)	Ref.
7.5Cr/Al ₂ O ₃	600	20	—	C ₃ H ₈ /Ar = 1:4	62	89	1.24	~2	[29]
Cr20/Al ₂ O ₃	500	30	WHSV = 1.2	C ₃ H ₈ /He = 1:14	12.9	87.7	0.13	~4	[30]
	550	30	WHSV = 1.2	C ₃ H ₈ /He = 1:14	33.8	94.0	0.36	~4	[30]
	600	30	WHSV = 1.2	C ₃ H ₈ /He = 1:14	41.8	89.8	0.42	~4	[30]
CrZrO _x	550	10–60	—	C ₃ H ₈ /N ₂ = 2:3	~30	~85	—	0.8	[34]
Cr20/CMK-3	550	30	WHSV = 1.2	C ₃ H ₈ /He = 1:14	47.5	84.7	0.45	~4	[35]
	600	30	WHSV = 1.2	C ₃ H ₈ /He = 1:14	54.2	81.8	0.50	~4	[35]
Cr-1/SiO ₂	550	10	GHSV = 353	C ₃ H ₈ /Ar = 1:4	~65	72	—	~21	[38]
Cr-1/SiO ₂ -Al ₂ O ₃	550	10	GHSV = 353	C ₃ H ₈ /Ar = 1:4	—	~70	—	25	[39]
Cr-1/Al ₂ O ₃	550	10	GHSV = 353	C ₃ H ₈ /Ar = 1:4	—	~65	—	25	[39]
CrZr5	550	30	WHSV = 1.2	C ₃ H ₈ /He = 1:14	50.7	92.2	0.53	1	[41]
2.5Cr/Al	550	20	—	C ₃ H ₈ /Ar = 1:9	24	~95	0.26	~3	[45]
2.5Cr-Ni/Al	550	20	—	C ₃ H ₈ /Ar = 1:9	43	~95	0.46	~3	[45]
17.5Cr-2Ce-2K/Al	630	80	—	C ₃ H ₈ /N ₂ = 1:1	~57.6	~80	10.4	<1	[46]

^a WHSV: weight hourly space velocity (h⁻¹); GHSV: gas hourly space velocity (h⁻¹). ^b Initial propane conversion. ^c Defined as (weight of propylene formed)/(weight of catalyst × t(h)). ^d Total time of a single cycle/experiment.

ever, no crystalline Cr_2O_3 particles could be seen over the $\text{Cr}/\text{Al}_2\text{O}_3$ catalysts even when the Cr loading is up to 5%. Beak et al. [33] observed that the Cr species supported on mesoporous silica with a low Cr content were isolated Cr^{6+} and polymeric Cr^{6+} . When the Cr loading exceeds the value of $\text{Cr}/\text{Si} = 0.082$, a number of crystallite Cr_2O_3 particles would be formed. Until now, the preparation of CrO_x -based catalysts containing stable and pure Cr^{n+} species is still a great challenge.

Generally, isolated, unsaturated and/or clustered Cr^{3+} sites are regarded as the active sites in CrO_x -based catalysts for PDH reaction [36,37]. Fig. 1 shows the possible catalytic mechanism of PDH reaction over Cr^{3+} catalysts [38,39]. Typically, the propane adsorbed would be converted into a $\text{Cr}-\text{C}_3\text{H}_8$ $\eta^3\text{-H,H,H}$ adduct. Heterolytic activation of a C–H bond yields $\text{Cr}^{3+}-\text{C}_3\text{H}_7$ intermediate. Subsequently, the $\beta\text{-H}$ in $\text{Cr}^{3+}-\text{C}_3\text{H}_7$ intermediate would be transformed on Cr^{3+} to form $\text{Cr}^{3+}-\text{C}_3\text{H}_6$ hydride surface species. Then, propylene would be released and H_2 formed, completing the catalytic cycle (Fig. 1a). Besides, byproducts, including methane, ethane, and ethylene, would be formed during the PDH process due to cracking, deep dehydrogenation, and hydrogenation (Fig. 1b and 1c).

3.1.1. Effect of supports on CrO_x -based catalysts

A series of metal oxides (such as Al_2O_3 , SiO_2 , and ZrO_2) have been studied as supports of CrO_x catalysts [18,24,28–39]. In these CrO_x -based catalysts, the supports play an important role in determining the dispersion (such as isolated Cr^{n+} , oligomeric Cr^{n+} , and crystallite CrO_x species), states (such as Cr^{6+} , Cr^{5+} , Cr^{3+} , and Cr^{2+}), structure, and electronic properties of the Cr species, thus affecting their catalytic activity, stability, and anti-coking capability in the PDH process.

Among these, Al_2O_3 is the mostly used support owing to its low price, high thermal stability, good mechanical stability, and strong interactions with Cr species, which result in improved dispersion, high catalytic stability, and good regenerability of $\text{CrO}_x/\text{Al}_2\text{O}_3$ catalysts [18,24,28]. Alternatively, zirconia (ZrO_2) has been demonstrated to be another efficient support for Cr catalysts owing to its weak acidity and strong interactions with

CrO_x species. In some case, $\text{CrO}_x/\text{ZrO}_2$ catalysts exhibit comparable and/or higher activities than $\text{CrO}_x/\text{Al}_2\text{O}_3$ catalysts [34,40]. However, a great challenge for these two catalyst systems is the serious coke formation that significantly shortens the catalyst life.

Improving the porosity of CrO_x -based catalysts is a good way of improving their performance in PDH. It was reported that CrO_x species supported on mesoporous Al_2O_3 exhibited enhanced activity in the PDH process due to the presence of many mesopores and highly dispersed Cr species [29]. A series of highly ordered mesoporous $\text{Cr}/\text{Al}_2\text{O}_3$ and Cr-Zr-O catalysts with narrow pore size distributions were synthesized by nanocasting method using CMK-3 as a hard template [30,41], and the resulting ordered mesoporous $\text{CrO}_x/\text{Al}_2\text{O}_3$ and Cr-Zr-O catalysts exhibited enhanced resistances to deactivation in PDH, compared to those of CrO_x catalysts supported on commercial Al_2O_3 and bulk ZrO_2 . Besides, enhanced catalytic performance in PDH reaction was also achieved for CrO_x catalysts supported on ordered mesoporous carbons (CMK-3) [35]. Owing to the presence of highly ordered mesopores in $\text{Cr}/\text{Al}_2\text{O}_3$, Cr-Zr-O , and $\text{Cr}/\text{CMK-3}$ catalysts, local transport limitations can be avoided during the PDH process. Therefore, the prepared mesoporous Cr-based catalysts exhibit enhanced activity, selectivity, and stability in PDH.

Introducing secondary metal oxides into Al_2O_3 and/or ZrO_2 support is another efficient method of improving the performances of Cr-based catalysts in PDH, because it can decrease the acidity of the as-synthesized catalysts and affect the dispersion and states of the Cr species. Kim et al. [42] reported that the distribution of CrO_x species was strongly dependent on the Zr/Al ratio. The addition of a certain amount of Zr species ($\text{Zr}/\text{Al} = 0.07$) to Al_2O_3 could increase the amounts of active Cr^{3+} species and decrease α -chromia-alumina, thus increasing the activity of CrO_x -based catalysts. Furthermore, Sim et al. [43] found that the introduction of ZrO_2 in Al_2O_3 support could greatly suppress the formation of chromia/alumina solid solution, and thereby improve the activity and thermal stability of CrO_x -based catalysts.

Fig. 1. (a) Possible PDH process over Cr-1/SiO_2 . (b) Generation of byproducts (methane and ethylene) during the PDH process over the Cr-1/SiO_2 catalyst. (c) Formation of ethane over the Cr-1/SiO_2 catalyst during the PDH process. The numbers in parentheses are the Gibbs free energies of the corresponding intermediates, and those on the arrows are the Gibbs free energies of the transition states, normalized with respect to that of Cr-1/SiO_2 + propane. All the energies are given in kcal mol⁻¹ [38].

Indeed, a number of novel supports (such as mesoporous Al_2O_3 , mesoporous ZrO_2 , and $\text{Al}_2\text{O}_3\text{-ZrO}_2$) have been exploited for the preparation of Cr-based catalysts that exhibit enhanced performances in PDH. However, there are still some drawbacks, such as serious side reactions (cracking, deep dehydrogenation, and coke formation), with these catalysts. In particular, their catalytic activities decrease obviously after times-on-stream of only several hours, as shown in Table 1. The exploitation of new efficient supports for improving the stability of Cr-based catalysts is still a great challenge.

3.1.2. Effect of promoters on CrO_x -based catalysts

Although metal oxides (such as Al_2O_3 and ZrO_2) have been widely studied as supports for CrO_x catalysts, the stability of CrO_x -based catalysts is still too low. To improve their performances, promoters (such as K, Ce, Ni, and Sn) are introduced into the CrO_x -based catalysts [40,41,42–45]. After the addition, their structure and surface properties would be greatly changed, which would have a great influence on their catalytic performance in PDH.

Alkali metals such as K, Na, Ca, and Mg have been widely used as promoters to poison the acidic sites of heterogeneous catalysts, and thereby, improve their selectivity and stability in the PDH process. In the earlier studies on CrO_x -based catalysts, the widely used alkali metal was K [40,41]. K-modified (0.2%, 0.5%, or 1%) Cr–Zr–O catalysts exhibit enhanced propylene selectivity and resistance to coke deposition in PDH reaction, compared with pristine Cr–Zr–O [41]. It is revealed that the addition of a K species can greatly decrease the acidity of Cr–Zr–O catalysts, thus decreasing the deactivation rate and coke formation. However, the addition of K species would also poison some Lewis acid sites, which has a negative impact on the PDH process. Cutrufello et al. [40] found that the activity of $\text{CrO}_x/\text{ZrO}_x$ catalyst after addition of $\text{K} \geq 1$ wt% was almost zero for PDH reaction. This is due to the fact that the K species hinder the reduction of Cr^{6+} to the active Cr^{3+} species and decrease the Lewis acid sites of Cr^{3+} in $\text{Cr}^{3+}\text{-O}_2^-$ acid-base couples, which are the possible sites for propane activation. Alkali metals can poison some strong acid sites of the catalysts, and thereby, increase the selectivity and anti-coking capability of CrO_x -based catalysts in PDH. However, some of the Lewis acid sites would also be poisoned after the addition of alkali metals, which has a negative influence on the PDH process. The development of a selective promoter that improves the activity, selectivity, and anti-coking capability of CrO_x -based catalysts is still ongoing.

Transition metal species have also been studied as promoters for CrO_x -based catalysts. Different from alkali metals, transition metals have little influence on the acidic properties of CrO_x -based catalysts. However, they play an important role in influencing the dispersion, oxygen capacity, and surface properties of CrO_x -based catalysts, thus affecting their PDH performance. Cabrera et al. [44] reported that introducing a certain amount of Sn into the $\text{CrO}_x/\text{Al}_2\text{O}_3$ catalyst can greatly decrease the coking formation during the PDH process. It is revealed that the addition of Sn species results in an important change in the amount of oxidized Cr species, which improves the activity, selectivity, and stability of $\text{CrO}_x/\text{Al}_2\text{O}_3$ catalysts. Furthermore,

addition of Ni species can promote the formation of oligomeric Cr species and affects the valence of the surface Cr species present on supports, thus improving the performances of $\text{CrO}_x/\text{Al}_2\text{O}_3$ catalysts [45]. Besides, Ce, Sb, Co, and Bi have been added to $\text{CrO}_x/\text{Al}_2\text{O}_3$ catalysts [45–48]. The addition of these metal species can affect the oxygen capacity and magnetic properties of CrO_x -based catalysts, which can positively contribute to the PDH process.

In summary, the performances of CrO_x -based catalysts are strongly affected by the preparation methods, natures of supports and promoters, structures of catalysts, and active sites present in the catalysts. Generally, CrO_x catalysts supported on traditional supports (such as Al_2O_3 , SiO_2 , and ZrO_2) display small surface areas and pore volumes, and exhibit low catalytic stability in PDH reaction. To improve the catalytic performance, novel supports (such as SBA-15, ordered mesoporous Al_2O_3 , and mesoporous carbon) with ordered mesopores have been used for CrO_x catalysts. Ordered mesostructures of supports have the advantages of well-controlled morphologies, high surface areas, and rich pores, which are good for mass transportation and can provide more accessible active sites. However, syntheses of these supports are time-consuming, complex, and expensive, and cannot be widely employed in industry. Furthermore, the active sites and mechanisms of these catalysts are hard to identify owing to their heterogeneous structures in microfields. Alternatively, novel methods (such as surface-organometallic-chemistry method) have been used for the synthesis of isolated Cr catalysts. Owing to their well-defined structure, the catalytic mechanism could be easily identified. On the basis of the abovementioned advantages and disadvantages of CrO_x -based catalysts, it can be concluded that a good CrO_x -based catalyst in PDH reaction must contain well-defined pores (which aid mass transport), display a high surface area (i.e., supply more accessible active sites), and exhibit suitable acidity (to avoid cracking and deep dehydrogenation). Possibly, zeolites (with well-defined pores and controlled acidities) and mixed metal oxides (with high surface areas and low acidities) are promising supports for Cr catalysts in PDH reaction.

Furthermore, the addition of promoters (such as Li, Na, K, Sn, Co, and Ce) can strongly affect the performances of CrO_x -based catalysts in PDH. Alkali metals (such as Li, Na, and K) can curb the acidity of the support and suppress the formation of coke on the catalyst. However, some of the Lewis acid sites would be poisoned after the addition of alkali metals, which would result in a decrease in the catalytic activity. Alternatively, transition metals can be utilized as promising promoters for CrO_x -based catalysts. Transition metals can improve the distribution of Cr species, decrease the acidity of supports, moderate the surface properties of the Cr species, and have little influence on the Lewis acid sites of CrO_x -based catalysts, thus improving their activity, selectivity, stability, and anti-coking capability in PDH.

3.2. Pt-based catalysts

Pt-based catalysts are the most widely used PDH catalysts that have been commercially employed in Oleflex (UOP) craft

[21,23,49–51]. Compared with CrO_x -based catalysts, Pt-based catalysts display many advantages such as eco-friendliness and high stability. However, this catalyst system still suffers from deactivation and coke formation. Particularly, the sintering of Pt during the PDH would result in irreversible deactivation. Great efforts have been made to improve the activity and stability of Pt catalysts by loading them onto porous supports, which results in changes to several properties (such as dispersion, reducibility, structure, and electronic properties) of the Pt species that have a great influence on their performance. Table 2 lists the recently reported Pt-based catalysts for PDH reaction.

In Pt-based catalysts, the size and structure of the Pt nanoparticles can greatly influence their activity, selectivity, stabil-

ity, and the mechanism of the PDH process. Zhu et al. [52] synthesized a series of Pt nanoparticles with the sizes of 3–9 nm that were subsequently supported on $\text{Mg}(\text{Al})\text{O}$. It was found that the propane conversion of Pt catalysts decreased with increasing Pt particle size. Particularly, the Pt particles with small sizes and (211)-dominating crystal planes revealed a low dehydrogenation energy barrier and a high catalytic activity. On the other hand, large particles with Pt (111)-dominating crystal planes exhibited a high energy barrier for C–H bond activation. Besides, the composition of the carrier gas can influence the performances of Pt-based catalysts, because H_2 can decrease the coverage of deeply dehydrogenated coke precursors on the surface of active sites [53]. Thus, the generated propylene can be easily desorbed from the surface of Pt to

Table 2

Summary of the data of Pt-based catalysts for PDH.

Catalyst	Reaction temperature (°C)	Flow rate (mL/min)	Space velocity ^a (h^{-1})	Feed composition	Conversion ^b (%)	Selectivity ^c (%)	Space time yield ^d (h^{-1})	Catalyst life ^e (h)	Ref.
Pt-Sn/MgAl ₂ O ₄	575	76.15	WHSV = 14.7	C ₃ H ₈ /H ₂ = 5:4, balance Ar	~33–29	~99	4.58	3.3	[50]
Pt-Sn/ZSM-5	590	—	WHSV = 3.0	C ₃ H ₈ /H ₂ = 4:1	33.1–26.3	47.7–56.4	0.45	6	[54]
Pt-Sn/ γ -Al ₂ O ₃	590	—	WHSV = 3.0	C ₃ H ₈ /H ₂ = 4:1	29.4–22.7	~90	0.76	6	[54]
Pt-Sn/mesoporous Al ₂ O ₃	590	—	WHSV = 3.0	C ₃ H ₈ /H ₂ = 4:1	29.8–24.6	~90	0.77	6	[54]
Pt-Sn/SBA-15	590	—	WHSV = 3.0	C ₃ H ₈ /H ₂ = 4:1	~11.0–6.0	~90	0.28	6	[54]
Pt/Al ₂ O ₃ sheet	590	—	WHSV = 9.4	C ₃ H ₈ /H ₂ /N ₂ = 1:1.25:4	42.7–15.9	95.7	3.67	24	[55]
PtSn/Al ₂ O ₃ sheet	590	—	WHSV = 9.4	C ₃ H ₈ /H ₂ /N ₂ = 1:1.25:4	48.7–44.6	99.1	4.33	24	[55]
	590	—	WHSV = 56.5	C ₃ H ₈ /H ₂ /N ₂ = 1:1.25:4	28.9–27.2	99.5	15.5	24	[55]
2Pt-0.6Sn/ γ -Al ₂ O ₃	540	50	—	C ₃ H ₈ /H ₂ /N ₂ = 6:2:42	42.9–39.2	97.5	1.41	8	[57]
2Pt-1.2Sn/-Al ₂ O ₃	540	50	—	C ₃ H ₈ /H ₂ /N ₂ = 6:2:42	43.5–41.4	99.1	1.45	8	[57]
2Pt-2.4Sn/ γ -Al ₂ O ₃	540	50	—	C ₃ H ₈ /H ₂ /N ₂ = 6:2:42	42.8–41.7	99.4	1.44	8	[57]
2Pt-3.6Sn/ γ -Al ₂ O ₃	540	50	—	C ₃ H ₈ /H ₂ /N ₂ = 6:2:42	42.8–41.8	99.4	1.44	8	[57]
Pt/TiO ₂ -Al ₂ O ₃	600	50	WHSV = 10	C ₃ H ₈ /H ₂ /N ₂ = 13:13:24	47.3–25.9	92.2	4.16	10	[58]
Pt/Mg(Zn)AlO _x	550	—	WHSV = 8	C ₃ H ₈ /H ₂ = 4:1	19	~99.3	1.44	—	[60]
PtIn/Mg(Al)O-x	620	—	WHSV = 3.3	C ₃ H ₈ /H ₂ /Ar = 8:7:35	66.4–43.5	95	1.99	8	[62]
Pt/CeAl	600	50	WHSV = 10	C ₃ H ₈ /H ₂ = 1:1, balance N ₂	47.1–22.2	86.0	3.87	15	[63]
Pt3Ga/Al ₂ O ₃	600	50	WHSV = 10	C ₃ H ₈ /H ₂ = 1:1, balance N ₂	39.4–28.1	99.5	3.74	15	[63]
Pt3Ga/CeAl	600	50	WHSV = 10	C ₃ H ₈ /H ₂ = 1:1, balance N ₂	41.1–32.2	99.6	3.91	15	[63]
PtSnIn/08Zr-Al	600	—	WHSV = 3.3	C ₃ H ₈ /H ₂ /Ar = 8:7:35	55.0	98.0	1.70	2.5	[64]
PtSnAl _{0.2} /SBA-15	590	—	WHSV = 2.5	C ₃ H ₈ /Ar = 1:5	55.9–40.5	98.5	1.31	6	[66]
Pt-Sn/SAPO-34-500	595	—	WHSV = 5.6	C ₃ H ₈ /H ₂ = 4:1	34.63	93.11	1.72	8	[67]
PtNa/Zn(1.0%)-ZSM-5	590	—	WHSV = 3.0	C ₃ H ₈ /H ₂ = 4:1	40.6	~96	1.12	10	[68]
PtSn/TS-1	600	—	WHSV = 3	C ₃ H ₈ /H ₂ /N ₂ = 1:1:4	53.5–47.7	~92.5	1.42	7	[20]
Pt-Sn-2/MgAl ₂ O ₄	580	20	—	C ₃ H ₈ /H ₂ /He = 1:1:8	45–18.7	94–98.3	0.95	90	[74]
Pt-Sn-3/MgAl ₂ O ₄	580	20	—	C ₃ H ₈ /H ₂ /He = 1:1:8	18.7	98.3	0.41	90	[74]
Pt-Sn-4/MgAl ₂ O ₄	580	20	—	C ₃ H ₈ /H ₂ /He = 1:1:8	31.5	99.6	0.71	90	[74]
Pt-Sn-5/MgAl ₂ O ₄	580	20	—	C ₃ H ₈ /H ₂ /He = 1:1:8	45–37.6	99.5	1.01	90	[74]
Pt-Sn-6/MgAl ₂ O ₄	580	20	—	C ₃ H ₈ /H ₂ /He = 1:1:8	45–38.9	99.7	1.01	90	[74]
0.5 wt%Pt/Mg(Sn)(Al)O	550	—	WHSV = 14	C ₃ H ₈ /H ₂ /Ar = 1:0.5:2	29.4–27.8	93.7–99.2	3.68	240	[75]
	600	—	WHSV = 14	C ₃ H ₈ /H ₂ /Ar = 1:0.5:2	48.3–43.0	86.4–98.1	5.57	48	[75]
Pt/0.5Sn-SBA-15	580	—	WHSV = 8.25	C ₃ H ₈ /Ar = 7:3	43.8	98.5	3.40	6	[77]
Pt-Sn/SiO ₂ -1073 K H ₂	500	100	WHSV = 47	C ₃ H ₈ /N ₂ = 1:4	27.0	99.5	12.1	3	[80]
15%Zn-0.1%Pt/Al ₂ O ₃	600	50	WHSV = 3	C ₃ H ₈ /H ₂ = 1:1, balance N ₂	35–31	94–97	0.94	4	[84]
0.3PtSn/1.5In-Al	620	—	GHSV = 1500	C ₃ H ₈ /H ₂ /Ar = 8:7:35	58.4–48.6	92.8	—	2.75	[90]
PtIn/Mg(Al)O-600	620	—	WHSV = 3.3	C ₃ H ₈ /H ₂ /Ar = 8:7:35	69.0	98.0	2.13	30	[91]
Ga ⁶⁺ Pt ⁰ /SiO ₂	550	50	WHSV = 98.3	C ₃ H ₈ /Ar = 1:4	31.9–18.2	99	29.6	20	[19]
	550	50	WHSV = 43.3	C ₃ H ₈ /Ar = 1:4	36.5–26.9	90.9–82.8	13.71	20	[19]
	550	50	WHSV = 2.0	C ₃ H ₈ /Ar = 1:4	40.7–38.5	63.5–70.1	0.49	20	[19]
0.1Pt10Cu/Al ₂ O ₃	520	50	WHSV = 4	C ₃ H ₆ /H ₂ /N ₂ = 4:4:17	13.1	90	0.45	120	[92]
Pt-Cu/MgAl ₂ O ₄	580	40	WHSV = 6.8	C ₃ H ₆ /H ₂ /Ar = 19:19:1	25.7–21.0	87.5–93.1	1.46	24	[95]
Pt-Ag/MgAl ₂ O ₄	580	40	WHSV = 6.8	C ₃ H ₆ /H ₂ /Ar = 19:19:1	30.6–16.7	85.1–95.0	1.69	24	[95]
Pt-Au/MgAl ₂ O ₄	580	40	WHSV = 6.8	C ₃ H ₆ /H ₂ /Ar = 19:19:1	33.7–16.6	60.0–88.2	1.31	24	[95]

^a WHSV: weight hourly space velocity (h^{-1}); GHSV: gas hourly space velocity (h^{-1}). ^{b,c} The first value is obtained at the start of the cycle, and the second at the end. ^d Defined as (weight of propylene formed)/(weight of catalyst $\times$ t(h)). ^e Total time of a single cycle/experiment.

avoid side reactions such as cracking and coke formation.

3.2.1. Effect of supports on Pt-based catalysts

In Pt-based catalysts, the support plays an important role in determining the dispersion, stability, and structural and electronic properties of the Pt particles. During the PDH process, the high reaction temperature would result in the growth of Pt particles, which would have a negative impact on the PDH process. Therefore, a good support for Pt-based catalysts should stabilize the Pt species. A number of supports (such as Al_2O_3 , SiO_2 , $\text{TiO}_x\text{-Al}_2\text{O}_3$, MgAl_2O_4 , $\text{Mg}(\text{Zn})\text{AlO}_x$, $\text{Mg}(\text{Ga})(\text{Al})\text{O}$, mixed oxides, zeolites, and nanocarbons) have been studied for PDH catalysts [19–20,49–95].

Among these, Al_2O_3 is the mostly used support for Pt catalysts owing to its high thermal stability, rich pores, low price, and high mechanical strength. Zhang et al. [54] investigated the influences of different supports (ZSM-5, $\gamma\text{-Al}_2\text{O}_3$, mesoporous alumina, and SBA-15) on the performances of Pt-Sn catalysts in PDH. It was found that Pt-Sn supported on $\gamma\text{-Al}_2\text{O}_3$ and mesoporous alumina exhibit high catalytic activities and selectivities for PDH. However, Pt-Sn supported on SBA-15 and HZSM-5 display really low activities and selectivities, respectively. This is due to the presence of a weak interaction between SBA-15 and Pt-Sn. In particular, the high acidity of HZSM-5 would result in cracking and deep dehydrogenation, which have a negative influence on PDH. To improve the interactions between Pt and the Al_2O_3 support, some novel and/or modified Al_2O_3 supports are used for the preparation of Pt-based catalysts. Shi et al. [55] synthesized Al_2O_3 nanosheets with pentacoordinate Al^{3+} as supports for Pt-Sn clusters. The pentacoordinate Al^{3+} species can well disperse and stabilize raft-like Pt-Sn clusters, and guarantees high activity and stability. However, Al_2O_3 exhibits a high acidity, which can lead to deep dehydrogenation, cracking, and coke formation [56,57].

In order to decrease the acidity of Al_2O_3 , a non-acidic metal oxide needs to be introduced. It is reported that the addition of TiO_2 species to Al_2O_3 support can improve the stability of Pt-based catalysts. The introduction of TiO_2 can increase the electron density of Pt, and thus, reduce the adsorption of propylene and improve the stability [58]. Alternatively, MgO species can be introduced into Al_2O_3 support. Shan et al. found that Pt-Sn supported on MgAl_2O_4 exhibited high catalytic activity and long-term stability for PDH owing to the hierarchical structure and weak acidity [50]. Furthermore, $\text{Mg}(\text{Ga})(\text{Al})\text{O}$ [59], $\text{Mg}(\text{Zn})\text{AlO}_x$ [60], Mg , Al , In -containing layered double hydroxides [61], and $\text{In}/\text{Mg}(\text{Al})\text{O}-x$ [62] materials are used as supports in the preparation of Pt-based catalysts that exhibit enhanced catalytic stability and anti-coking capability for PDH. This is due to the changes in the structure, acidity, surface, and electronic properties of Pt-based catalysts. Particularly, the decrease in the acidity of the support is good for the desorption of the product propylene, and thus, leads to enhanced catalytic stability and anti-coking capability. Additionally, other metal oxides (such as CeO_2 , ZrO_2 , and SiO_2) are also introduced into Al_2O_3 support [63–66]. After mixing with these metal oxides, the activity, stability, and anti-coking capability of Pt-based catalysts would be greatly improved, due to the increased in-

teractions between Pt and the supports, which improve the dispersion, decrease the acidity, and moderate the electronic properties of Pt catalysts.

Zeolites have been reported as promising supports for Pt-based catalysts for PDH owing to their well-defined pores, high surface areas, and tunable acidities. Nawaz et al. [67] reported that Pt-Sn supported on SAPO-34 exhibited a high catalytic activity for PDH. However, calcination temperature can affect the performance of Pt-based catalysts. After calcination at high temperatures, the structure of SAPO-34 would be changed, which leads to a decrease in the catalytic activity. Alternatively, ZSM-5 zeolites display high thermal stability, and can be used as a promising support for Pt species. Zhang et al. [68] reported that Pt supported on Zn-modified ZSM-5 exhibited high activity and stability for PDH. However, the high acidity of ZSM-5 support leads to serious cracking and coke formation. To decrease the acidity of ZSM-5, TS-1 zeolites with different particle sizes are synthesized and used as a support for Pt-Sn catalysts [20]. The resulting Pt-Sn/TS-1 catalysts exhibit high activity and long-term stability in PDH. Fig. 2 shows the performances of Pt-Sn catalysts supported on TS-1 zeolites with different particle sizes. It can be seen that the TS-1 zeolites with smaller particle sizes that supported Pt-Sn catalysts exhibit higher catalytic performance. For comparison, Pt-Sn catalysts supported on HZSM-5 were synthesized, which reveal really low propylene selectivity and stability, compared to those of Pt-Sn/TS-1 catalysts. This is due to the TS-1 zeolite with a smaller particle size displaying a hierarchically porous structure, high surface area, and low acidity, which are good for mass transport, Pt-Sn dispersion, and propylene desorption. However, owing to the presence of weak interactions between Pt-Sn and TS-1, the regeneration stability of Pt-Sn/TS-1 catalyst is really low (Fig. 2d).

Over the last several years, some articles have reported a number of Pt/zeolite catalysts that exhibited high performances in PDH. However, the utilization of zeolites as supports of Pt-based catalysts in PDH is still a great challenge owing to their high acidity, which results in side reactions such as cracking and deep dehydrogenation. Furthermore, the weak interaction between Pt and zeolite would lead to the growth of the Pt particles during the PDH process.

Nanocarbons have also been used as supports in the preparation of Pt-based catalysts [69–71]. Volynkin et al. investigated four different nanocarbon (namely, carbon black, carbon nanofibers, carbon nanotubes, and graphite)-supported Pt-based catalysts for the PDH reaction [69]. It was found that Pt nanoparticles supported on carbon black exhibited the highest activity. This is probably due to the presence of different metal-support interactions between Pt and the carbon supports. Liu et al. reported that Pt supported on nanodiamond@graphene (ND@G) revealed high catalytic stability for PDH [70]. The presence of strong metal-support interactions can significantly prevent the Pt species from sintering and promote the desorption of propylene. After 100 h time-on-stream, only a slight loss in the activity can be observed for the Pt/ND@G catalyst. Later, Liu et al. [71] reported a defect-driven Pt/CNTs catalyst for PDH. Owing to the pres-

Fig. 2. (a) Propane conversion, (b) propylene selectivity, (c) TOF of propane conversion, and (d) cycle testing of PtSn/TS-1 as functions of reaction time. Note that *x* represents different crystal sizes: 100 nm (1), 201 nm (2), 305 nm (3), 650 nm (4), 1.10 μm (5), and 5.72 μm (6) [20].

ence of strong interactions between the Pt species and the defects of CNTs, the as-synthesized Pt/CNTs catalyst exhibits high activity, stability, and anti-coking ability in PDH. However, regeneration of this catalyst system is a critical issue that needs to be addressed.

In summary, supports play an important role in determining the performances of Pt-based catalysts in PDH. Generally, a good support for Pt-based catalysts should display a high surface area and good thermal stability. Al_2O_3 is a widely used support in Pt-based dehydrogenation catalysts. However, the high acidity of Al_2O_3 would result in serious cracking and coke formation. Introducing a non-acidic metal oxide (such as SiO_2 , MgO , or TiO_2) into Al_2O_3 has been considered as a very promising method of improving the performance of Pt- Al_2O_3 -based catalysts, because the introduction of metal oxides can decrease the acidity and increase the stability of Pt catalysts. Furthermore, this method has the advantages of easy operation, low cost, and high efficiency, and can be widely used in the preparation of Pt-based catalysts. Besides, some novel supports (such as zeolites and nanocarbons) have been employed for Pt catalysts. However, the high acidity of zeolites (which results in cracking and low selectivity) and the difficult regenerability of nanocarbons limit their widespread application.

3.2.2. Effect of promoters on Pt-based catalysts

Generally, a pure Pt catalyst exhibits a really low perfor-

mance in PDH [51,52]. In industry, the commercially utilized Pt-based catalysts are based on Pt-Sn/ Al_2O_3 , rather than on Pt/ Al_2O_3 . A number of studies have reported that the addition of promoters can greatly improve the dispersion and structural and electronic properties of Pt-based catalysts [19–21,23,54–68], thus improving their activity, selectivity, stability, and anti-coking capability in the PDH process.

Up to now, the widely used promoter is Sn. During the H_2 pretreatment process, a Pt-Sn alloy would be formed [72]. Density functional theory (DFT) reveals that propylene would be deeply dehydrogenated on the Pt particles. After the formation of the Pt-Sn alloy, the dehydrogenation barrier of the propylene on the Pt-Sn alloy is much higher than that of the propylene on Pt particles, which results in enhanced selectivity, stability, and anti-coking capability [73]. However, there are many phases present such as Pt_3Sn , Pt_2Sn_3 , PtSn , and PtSn_4 in the as-prepared Pt-Sn catalysts. Particularly, the Pt/Sn ratios and the positions of Sn would have great influences on the performances of Pt catalysts. Zhu et al. [74] developed a surface organometallic method for the synthesis of Pt-Sn nanoparticles with surface-enriched Sn, which were supported on MgAl_2O_4 and used for PDH; these catalysts exhibited high catalytic activity and long-term stability (Fig. 3). This is due to the high concentration of inactive Sn on the surface of the Pt nanoparticles, which results in many isolated active Pt atoms (Fig. 3a–3c). Furthermore, the Pt/Sn ratio can greatly influence the activity

Fig. 3. (a) TEM, (b) HAADF-STEM, and (c) EELS line scans of Pt-Sn particles. (d) Propane conversions and (e) propylene selectivities of different Pt-Sn/MgAl₂O₄ catalysts [74].

and anti-coking capability of Pt-Sn/MgAl₂O₄ catalysts. With increasing Sn/Pt ratio from 0 to 2:1, the activity and anti-coking capability of Pt-Sn/MgAl₂O₄ catalysts increase obviously (Fig. 3d–3e). Another study reported a highly selective and durable Pt-Sn catalyst for PDH, in which the active Pt clusters were confined by the lattice of Sn(IV/II), forming a number of highly stable raft-like Pt clusters [75]. The resulting Pt/Mg(Sn)(Al)O catalysts exhibit high activity and long-term stability in the PDH reaction. For 240 h time-on-stream at 550 °C, the conversion decreases at the rate of only 0.0067% h⁻¹, which is suggestive of a very promising PDH catalyst. Furthermore, a number of supported Pt-Sn catalysts (such as Pt-Sn/Al₂O₃ [56,57,76], PtSn/Al₂O₃/SBA-15 [65,66,77], PtSnNa@SUZ-4 [78,79], and Pt-Sn/SiO₂ [80]) have been synthesized and used in PDH. The utilization of Sn as a promoter can greatly improve the activity, stability, and anti-coking capability of Pt-based catalysts.

Zn is another widely used promoter in Pt-based catalysts. After the addition of Zn, the surface, structural, geometric, and electronic properties of Pt catalysts would be greatly changed. Zhang et al. [68] reported that Pt supported on Zn containing ZSM-5 exhibited enhanced catalytic activity and stability in PDH. The addition of Zn can poison the strong acidity of ZSM-5 zeolite and simultaneously improve the dispersion of Pt species, avoiding side reactions (such as cracking, deep dehydrogenation, and coke formation). PtZn alloy would be formed during the H₂ pretreatment, which would also be good for improving the catalytic activity and stability [81]. Cybulska et al. [82] reported that the Zn species could affect the geometric and electronic properties of the Pt species. It was found that the surface electronic structure and valence orbitals at the active metal sites can be tuned by using Zn promoters. Particularly,

the formation of Pt₁Zn₁ intermetallic alloy with uniformly isolated Pt surface sites can suppress the rates of structure-sensitive reactions (such as cracking and hydrogenolysis). Furthermore, the addition of Zn can decrease the energy of the filled states of the Pt surface, and weaken the formation of bonds between the 5d orbitals and adsorbates. Belskaya et al. [60] reported that the addition of Zn could affect the structural parameters, textural characteristics, and acid-base properties of the corresponding mixed oxides, which would have great influences on the performances of Pt/Mg(Zn)AlO_x catalysts. The structure and the strength of the interactions between Pt and supports are strongly dependent on the Zn content. The addition of Zn can decrease the particle size of the active metal and improve the stability of Pt particles, thereby ensuring high activity and selectivity. Very recently, Chen and coworkers [83] reported that Pt-Zn supported on high-silica HZSM-5 exhibit high catalytic activity and excellent stability in PDH. The framework Zn species in HZSM-5 zeolite can improve the dispersion and stability of Pt particles, and thus, increase the stability of Pt catalysts. On a different note, Gong's group [84] reported that ZnO is an active site for the PDH reaction. After doping only a small amount of Pt, the Lewis acid sites of ZnO would be greatly increased. Thus, the catalytic activity of ZnO/Al₂O₃ can be greatly increased. Indeed, single Zn²⁺ supported on SiO₂ were reported to be active for alkane dehydrogenation [85–87]. Up to now, the active sites of Pt-Zn catalysts for PDH are still debated.

It is reported to be a good promoter for Pt-based catalysts in PDH. Zha et al. [88] compared the catalytic performances of Pt, Pt₃In, and Pt₃Sn in PDH by using DFT. It is found that Pt₃In displays an activity that is comparable to those of Pt and Pt₃Sn,

but its selectivity towards propylene is higher than that of Pt. This is due to an apparent increase in electron transfer from In to Pt. Therefore, the adsorption energy of propylene would be moderated after the addition of In. Sun et al. [89] prepared a series of Pt/Mg(In)(Al)O catalysts for PDH. Upon reduction in H_2 , PtIn alloy with particle size of 1 nm would be formed. Furthermore, the content of In in the PtIn alloy increases with increases in the reduction temperature and In/Pt ratio. X-ray absorption near edge structure (XANES) reveals increasing transfer of electronic charges from In to Pt with the increase in the In content, which greatly influences the performance of Pt/Mg(In)(Al)O catalysts. When the In/Pt ratio is 0.48, Pt/Mg(In)(Al)O catalyst exhibits the highest activity, with a propylene selectivity of ~100%. Particularly, coke deposition is greatly reduced after the addition of the In species. It is also found that the coke produced on the surface of the PtIn particles can migrate to the support during the PDH process, which ensures high catalytic stability and anti-coking capability. Liu et al. [90] found that the addition of In can decrease the acidity of PtSn/Al₂O₃ catalysts, and thus, decrease cracking and coke formation. Furthermore, metallic In and PtIn alloy would be formed during H_2 pretreatment, which can improve the activity and selectivity of Pt-based catalysts. Shen et al. [91] reported that the calcination temperature can affect the performance of PtIn/Mg(Al)O catalysts. After calcination at high temperatures, the flake structure of PtIn/Mg(Al)O catalysts would collapse. A high calcination temperature would lead to the growth of metal particles, which is undesirable for the PDH reaction.

In addition, Ga, Cu, Mn, Fe, Co, Ni, and Ag have been studied as promoters for improving the performance of Pt-based catalysts in recent years. Copéret's group [19] developed a surface organometallic chemistry method to synthesis nanometric Ga-Pt bimetallic particles that exhibited high activity, selectivity, and stability in PDH. During the preparation process, the Pt precursor [Pt(OSi(O*t*Bu)₃)₂(COD)] could be grafted onto the surface of SiO₂ containing Ga single sites ((≡SiO)₃Ga(HOSi≡)). The XANES patterns reveal that electrons can transfer from the metallic phase of Ga to the Pt 5d band. The addition of Ga can greatly modify the electronic structure of the Pt species, and thus, improve the activity, selectivity, and stability of Pt-based catalysts. Gong's group [92] prepared a highly stable Pt/Cu single-atom alloy by coimpregnation method with a high Cu/Pt ratio (Fig. 4). It was found that the single Pt atoms are highly dispersed on the Cu nanoparticles, which dramatically enhances the desorption of propylene and prohibits its further dehydrogenation (Fig. 4a–4e). The resulting Pt/Cu catalysts exhibit high PDH stability of more than 120 h at 520 °C (Fig. 4f and 4g). Subsequently, they developed a well-defined Pt-skin catalyst that was modified by using different 3d transition metal atoms. The propylene selectivity was found to follow the order Pt < PtNi@Pt < PtCo@Pt < PtFe@Pt, which was in line with the trend calculated for the shifting of the *d*-band center [93]. Wu et al. [94] reported that the addition of Mn to Pt could change the catalytic and adsorption properties of Pt-based catalysts. When Pt-based catalysts contain a Pt₃Mn subsurface, they exhibit a higher selectivity towards C–H bond activation than towards C–C bond activation during the PDH process. The for-

mation of Pt₃Mn phase can significantly reduce the heat of adsorption of the reactant, thus improving the activity and stability of Pt catalysts. Zhang's group [95] investigated the influence of group IB metals (Cu, Ag, and Au) on Pt/MgAl₂O₄ catalysts. It was found that Pt-Cu/MgAl₂O₄ catalyst exhibits excellent propane yield and regeneration stability, presumably owing to the formation of intermetallic compounds and little phase segregation during the cyclic dehydrogenation-regeneration runs.

In the PDH process occurring over Pt-based catalysts, a supported pure Pt catalyst usually exhibits low activity and selectivity. After the introduction of promoters (such as Sn, In, Zn, Cu, Mn, and Fe), the performance of Pt-based catalysts can be significantly increased, owing to the great improvements in the dispersion and structural and electronic properties of the Pt catalysts. Among these promoters, Sn, Zn, and In are the ones that are widely used for Pt catalysts. Sn and Zn can hinder side reactions such as isomerization and coke formation during alkane dehydrogenation, whereas In can prevent side reactions by poisoning the Brönsted acid sites; the formation of Pt-In alloy has electronic and geometric effects on the Pt species, which decrease the coke formation. With the development of Pt catalysts, many other transition metals (such as Cu, Ag, and Fe) have been found to be good promoters for Pt-based catalysts. Particularly, single Pt atom and/or alloy Pt-*M* atoms (*M* = Cu, Ag, Fe, etc.) can be synthesized and utilized as catalysts in PDH. These provide great opportunities for the utilization of Pt species at the atomic scale. Owing to the presence of atomic Pt species, these catalysts exhibit the advantages of high stability and anti-coking capability, which make them a type of highly promising industrial PDH catalyst.

3.3. Vanadium oxide-based catalysts

Supported vanadium oxides (VO_x) are reported to be one of the most promising alternative catalysts to Pt- and CrO_x-based catalysts in PDH, owing to their low price and high catalytic activity. In fresh VO_x-based catalysts, there are many kinds of V species present, such as V⁵⁺, V⁴⁺, V³⁺, isolated V, oligomeric V^{*n*+}, and crystalline V₂O₅ [96–104]. Furthermore, V⁵⁺ species would be transformed into V⁴⁺ and/or V³⁺ during the PDH process due to the presence of H₂.

Generally, the nature of the V species is strongly dependent on the type of support, V loading amount, and preparation method. Sokolv et al. [97] reported that the type of support (Al₂O₃, SiO₂ (MCM-41), and Al₂O₃-SiO₂) can greatly influence the activity and stability of VO_x-based catalysts in PDH. VO_x supported on Al₂O₃-SiO₂ with 70% SiO₂ exhibited excellent ability to restore the initial activity, as proven through a series of 10 dehydrogenation/oxidative regeneration cycles. Further, the tendency of the catalyst to form coke increases with the increase in the surface acidity. Later, they pointed out that VO_x species were more active for coke formation than the acid sites of the supports [98]. The rate constant of carbon formation increases with the degree of polymerization of VO_x species. Liu et al. [99] reported that the V³⁺ in VO_x/Al₂O₃ catalysts were the most probable active sites in PDH (Fig. 5). Particularly, the V loading amount can influence the types of V species present in

Fig. 4. (a) HAADF-STEM images of reduced 0.1Pt10Cu/Al₂O₃ catalyst. (b, c) Enlarged image and colored intensity map obtained for the region selected in (a). (d) Relative stability of Pt single atoms over Cu (~2.1 nm) nanoparticles: dark red indicates a stable location of Pt atom. The unit of the color bar is eV/Pt atom. (e) HAADF-STEM image of a typical region of the reduced 10Cu/Al₂O₃ catalyst, showing no Pt atoms existing on the surface of the Cu nanoparticles. (f) Catalytic performances at the initial and final stages at 520 °C and 550 °C for 12 h PDH, showing significantly improved performances of Pt/Cu single atom alloys, compared with those of Pt nanoparticles. (g) Long-term stability test results of 0.1Pt10Cu/Al₂O₃ at 520 °C for 120 h. The scale bars correspond to 1 nm in (a), (b), (c), and (e) [92].

VO_x/Al₂O₃ catalysts. At a low V loading (V/Al = 1.0), isolated V species are mainly dispersed on the Al₂O₃ support. With increasing V loading up to V/Al = 1.4, some polymerized VO_x species would be formed. When the V loading is higher than V/Al = 1.6, crystallite V₂O₅ would be formed. Turnover frequency (TOF) result suggests that isolated V³⁺ species are more active than the other V sites (such as V⁵⁺, V⁴⁺, and V₂O₅) in the PDH process. *In situ* diffuse reflectance infrared Fourier transform (DRIFT) spectra (Fig. 5b and 5c) reveal that V-C₃H₅ is formed during the PDH process. This indicates that propane activation over the catalyst surface involves the abstraction of a H atom, and the formed vanadium propyl is then rapidly transformed into V-C₃H₅. Furthermore, the preparation conditions can have a great influence on the performance of VO_x catalysts. Hu et al. [100] reported that the gelation and calcination temperature could greatly influence the structure and performance of VO_x-SiO₂ catalysts. At the gelation temperature of 60 °C and calcination temperature of 580 °C, the obtained 60-VO_x-SiO₂-580 catalyst exhibits high activity for PDH. How-

ever, higher gelation (≥75 °C) and calcination temperatures (>580 °C) would result in decreased catalytic performance, owing to the high temperature influencing the structural properties of VO_x-SiO₂ catalysts.

Improving the structural properties of VO_x-based catalysts is good for mass transport and can provide more accessible active sites. The VO_x species supported on mesoporous Al₂O₃ exhibits high catalytic performance in PDH [101]. Mesoporous Al₂O₃ favors the formation of polymerized VO_x species, which are more active than isolated V species in PDH. Alternatively, mesoporous silica can be used as a support for VO_x. Rodemerck et al. [102] reported that VO_x species supported on MCM-41 exhibited high catalytic performance in PDH. It was found that isolated VO_x species are more active than their oligomerized counterparts, which is in good agreement with Gong's report [99]. To decrease the acidity of VO_x-based catalysts, non-acidic metal oxides are introduced into VO_x catalysts. Wu et al. [103] reported that MgO-modified VO_x/Al₂O₃ exhibited enhanced stability, compared with that of pristine VO_x/Al₂O₃. This is due

Fig. 5. (a) Proposed surface model of VO_x/Al₂O₃ catalyst. (b) DRIFT spectra observed for the reaction of propane over 12V/Al catalyst after (1) propane adsorption at 30 °C, (2) subsequent heating at 300 °C for 60 min, and (3) evacuation at 30 °C. (c) DRIFT spectra observed after (1) adsorption of propylene at 30 °C, (2) heating at 200 °C under H₂/Ar for 30 min, (3) subsequent evacuation at 30 °C, and (4) heating the sample with adsorbed propylene at 200 °C under He over the 12V/Al catalyst [99].

to the addition of MgO, which improved the dispersion of V species and decreased the acidity of the catalyst, thereby decreasing the coke formation and improving the stability of VO_x/Al₂O₃ catalyst. Furthermore, some methods have been reported for improving the performance of VO_x-based catalysts. Zhao et al. [104] proposed a H₂ reduction method to increase the amount of hydroxyl species on VO_x/Al₂O₃ catalysts. After pretreatment in H₂ for only several minutes, the obtained VO_x/Al₂O₃ exhibited enhanced catalytic stability in PDH.

Up to now, a number of studies have investigated many efficient VO_x-based catalysts. In some cases, their performances are comparable to those of Pt- and CrO_x-based catalysts. However, the low stability and bad regenerability of VO_x-based catalysts limit their widespread application. Initially, the strong adsorption of propane onto the active sites would lead to coke formation. When the coke is removed by calcination of the catalyst in an oxidizing atmosphere, the V species tend to aggregate into large crystallite V₂O₅ particles, which are inactive in the PDH reaction. Furthermore, there are many V species (such as V⁵⁺, V⁴⁺, V³⁺, isolated V, oligomeric Vⁿ⁺, and crystalline V₂O₅) that are present on VO_x-based catalysts. The role of each V species in PDH is still debated.

3.4. Gallium oxide-based catalysts

Gallium oxide (GaO_x)-based catalysts have been studied for PDH reaction for years. Particularly, the nature of Ga species is strongly affected by the types of supports, preparation methods, and loading amounts. Zheng et al. [105] reported the presence of many different polymorphs of gallium oxides in supported GaO_x catalysts. Particularly, β-Ga₂O₃ exhibits the highest activity among all the polymorphs [96]. Shao et al. [106] reported that GaO_x supported on different supports (ZSM-5, SBA-15, γ-Al₂O₃, and SiO₂) with different Ga amounts exhibited different catalytic performances in PDH. Catalysis and characterization results reveal that GaO_x supported on ZSM-5 and SBA-15 exhibit high performances owing to the good dispersion of Ga species. By adjusting the Ga loading on SBA-15, it is found that Ga₂O₃/SBA-15 with 5 wt% Ga₂O₃ displays the best catalytic performance owing to its high surface area, well-dispersed GaO_x species, and low acidity. Similarly, Chen et al. [107] found that the Ga/Al ratio would affect the acidity properties of spinel-type Gallia-alumina solid solution catalysts (Ga_xAl_{10-x}O₁₅ oxides), which influence their catalytic performance in PDH. When Ga/Al is 4:1, the oxide Ga₄Al₂O₁₅ exhibits the highest catalytic activity. In particular, the formation of spinel-type γ-Ga₂O₃-Al₂O₃ solid solution plays an important role in the distribution and dispersion of surface Ga species, which renders Ga_xAl_{10-x}O₁₅ composites highly active and stable in

PDH.

Some novel methods have been explored for improving the performance of Ga catalysts. Searles et al. [108] and Szeto et al. [109] developed a surface organometallic method to synthesize Ga-1/Al₂O₃, Ga-2/SiO₂, and Ga-1/SiO₂ catalysts (Fig. 6). Through the reaction between the Ga precursors and Al₂O₃, SiO₂, and/or Si containing precursors, Ga-based catalysts with single and/or double Ga atoms can be synthesized. The results suggest that the Al₂O₃-supported catalyst exhibits promising activity and high selectivity toward propylene. These studies provide a new strategy to synthesize single and/or double Ga atom catalysts.

Additionally, GaO_x species supported on zeolites with MFI structure are widely reported [110–115]. After the Ga species are supported on zeolites, their dispersion, structure, and electronic properties would be greatly improved. Particularly, the types, acidities, and porous structures of zeolites would significantly influence the performance of Ga-zeolite catalysts. Ren et al. [110] reported that the acidity and pore geometry of the support would have a great influence on the performance of GaO_x-based catalysts. By adjusting the Si/Al ratio of HZSM-5, it is found that the activity of Ga₂O₃/HZSM-48 decreases with increasing Si/Al ratio, while the selectivity shows an opposite trend. Furthermore, it is found that the stability of Ga₂O₃/HZSM-48 is lower than that of Ga₂O₃/HZSM-5, which is probably due to the presence of abundant weak acid sites and unidimensional pore structure in HZSM-48. Kim et al. [111] prepared a series of hierarchical Ga-MFI catalysts. It is found that hierarchical Ga-MFI catalysts display greater Lewis acid sites than bulk catalysts, which exhibit better PDH performance. Additionally, Choi et al. [112] prepared a series of gallosilicate MFI zeolites with perturbed acidities, which exhibited high catalytic activity and stability. This is due to the reduced

Brønsted acidity and enhanced Lewis acidity of gallosilicate MFI zeolites. Lercher et al. [113] proposed a mechanism for Ga/HZSM-5 catalysts by which the Lewis–Brønsted acid pairs in Ga/H-ZSM-5 could catalyze the dehydrogenation of propane to propylene. DFT revealed that the high activity is attributed to a bifunctional mechanism that proceeds via heterolytic activation of the propane C–H bond, which is followed by monomolecular elimination of H₂ and desorption of propene. However, Mansoor et al. [114] remodeled Ga/H-MFI catalysts and found that univalent and divalent gallium hydrides, [GaH₂]⁺ and [GaH]²⁺, respectively, were more active for alkane dehydrogenation, in comparison to H⁺ and Ga⁺ sites. Particularly, [GaH]²⁺ are the most probable active sites for alkane dehydrogenation.

Furthermore, In₂O₃-Ga₂O₃ mixed oxides [116,117] have been synthesized and used in PDH, for which they exhibit a high catalytic activity. However, the activity and selectivity of GaO_x-based catalysts are still too low, compared with those of Pt- and CrO_x-based catalysts. Furthermore, GaO_x-based catalysts exhibit low stability and bad regenerability due to coke formation and the sintering of GaO_x species during the PDH reaction, which is similar to VO_x-based catalysts. Therefore, frequent regeneration (typically through calcination in air) is needed to recover the performance of GaO_x-based catalysts. However, the regeneration process would result in the growth of GaO_x particles, which would lead to irreversible deactivation. Besides, the catalytic mechanism and active sites of Ga species are unclear. Further studies and improvements in GaO_x-based catalysts for PDH are therefore required.

3.5. Nanocarbon catalysts

Nanocarbons (such as graphene, carbon nanotubes, mesoporous carbons, and activated carbons) are green materials that have drawn much attention owing to their high thermal, mechanical, and electrical properties, which have been studied for decades in adsorption, separation, electrochemistry, and heterogeneous catalysis [5–8,118–124]. In heterogeneous catalysis, nanocarbons impregnated with metal and/or metal oxides are usually used for electrocatalysis [125–128], photocatalysis [129,130], and photoelectrocatalysis [131,132]. For the recovery and recycling of metals, particularly noble metals, these supports can be burned off. Recently, many studies have reported that nanocarbons could be directly used as metal-free catalysts for PDH and exhibit activities comparable to those of noble metal and/or metal oxide catalysts [5–8,133–142]. Table 3 lists the recent studies on nanocarbons for PDH. In general, their catalytic performances are related to their surface functional groups, structural properties, defects, and electronic properties.

Owing to the various morphologies and structures, nanocarbon materials can be modified and/or activated by chemical and/or physical methods. Some heteroatoms (O, P, N, S, etc.) are doped into nanocarbon materials [5–8,143–149]. Fig. 7 shows the different O, N, and P functional groups that can be introduced into the nanocarbon structures. O-containing groups (such as ketones, carboxylic anhydrides, lactone, carboxylic acid, ether, and phenol) and P-containing groups (–P=O,

Fig. 6. (a) Grafting of Ga(*i*-Bu)₃ onto Al₂O₃-500 and SiO₂-700, which lead to structurally distinct surface species. (b) Synthesis of [(≡SiO)₃Ga(HOR)] (2, R = -Si(O*t*Bu)₃ or -*t*Bu) and its thermal transformation under high vacuum yielding [(≡SiO)₃Ga(XOSi≡)] (3, X = H or ≡Si) [108,109].

Table 3

Summary of the catalytic data of nanocarbons for PDH reaction.

Catalyst	S_{BET} (m^2/g)	Flow rate (mL/min)	Feed composition	Reaction temperature ($^{\circ}\text{C}$)	Conversion ^a (%)	Selectivity ^b (%)	Space time yield ^c (h^{-1})	Catalyst life ^d (h)	Ref.
OMC-1	624	40	$\text{C}_3\text{H}_8/\text{N}_2 = 1:19$	600	69.3–44.5	62.2–85.1	0.24	100	[133]
OMC-2	610	40	$\text{C}_3\text{H}_8/\text{N}_2 = 1:19$	600	65.7–39.3	70.6–88.6	0.26	100	[133]
HOMC	675	40	$\text{C}_3\text{H}_8/\text{N}_2 = 1:19$	600	20.1–10.3	66.1–78.5	0.06	50	[135]
COMC	758	40	$\text{C}_3\text{H}_8/\text{N}_2 = 1:19$	600	22.6–12.1	89.0–95.1	0.09	50	[135]
ND-1100	350	15	$\text{C}_3\text{H}_8/\text{He} = 1:49$	550	10.6	90	0.013	15	[136]
MCO	310	40	$\text{C}_3\text{H}_8/\text{N}_2 = 1:19$	600	32.9–21.2	66.3–86.6	0.12	50	[137]
PMC	679	20	$\text{C}_3\text{H}_8/\text{N}_2 = 1:19$	600	37.1	89.2	0.19	24	[138]
BMC	690	20	$\text{C}_3\text{H}_8/\text{N}_2 = 1:19$	600	33.9	87.2	0.17	24	[138]
NMC	908	20	$\text{C}_3\text{H}_8/\text{N}_2 = 1:19$	600	18.6	84.6	0.09	24	[138]
1%P/CMK-3	1338	20	$\text{C}_3\text{H}_8/\text{N}_2 = 1:19$	600	28	88	0.28	24	[139]
CMSC-3-700	1400	20	$\text{C}_3\text{H}_8/\text{N}_2 = 1:19$	600	41.3–24.7	88.6–93.5	0.21	10	[140]
BDAC-700	1078	20	$\text{C}_3\text{H}_8/\text{N}_2 = 1:19$	600	54.2–29.7	85.8–91.4	0.26	50	[141]
so-MWCNTs	134	20	$\text{C}_3\text{H}_8/\text{N}_2 = 1:19$	600	11.2–5.8	92.1–87.9	0.06	4	[142]

^{a, b} The first value is obtained at the start of the cycle, whereas the second is obtained at the end. ^c Defined as (weight of propylene formed)/(weight of catalyst $\times$ t (h)). ^d Total time of a single cycle/experiment.

–PO(OH)₂, –OPO(OH)₂ and –P(OH)₂ can be introduced into the nanocarbons by chemical oxidation [146–148,150–152]. N-containing groups (such as pyridine oxide, amide, amine, pyrrole, pyridine, and lactam) are usually synthesized by carbonization of a N-containing precursor or through reaction with a N-containing reagent [5–8,147–149]. Furthermore, other heteroatoms (B, F, Cl, etc.) can also be introduced into the nanocarbon materials by chemical oxidation and/or carbonization of a heteroatom-containing precursor [5–8]. After nanocarbon materials are doped with heteroatoms, their properties (such as electrical conductivity, porosities, and mechanical and chemical properties) would be significantly improved, which would greatly influence their catalytic performances.

Yuan's group [133] reported that ordered mesoporous carbons (OMCs) exhibited high catalytic activity and long-term stability in PDH. In this study, OMCs (OMC-1 and OMC-2) were prepared by a self-assembly method, where resor-

cinol/formaldehyde precursor and F127 template were mixed with ethanol/water acidic solution in a low-temperature autoclaving condition. The PDH results show that the initial propane conversions of OMC-1 and OMC-2 are 69.3% and 65.7%, respectively, at the reaction temperature of 600 $^{\circ}\text{C}$. After 100 h time-on-stream, the propane conversions of OMC-1 and OMC-2 decrease to 44.5% and 39.3%, with the propylene selectivities being 85.1% and 88.6%, respectively (Fig. 8). The stable propylene yield of OMC-1 is about 38%, which is comparable to that of CrO_x- and Pt-based catalysts [34,35,38–45,54–58,62–66]. For comparison, CNTs and commercial graphite carbon were tested for PDH, and these exhibited much lower catalytic activities than OMCs. This is probably due to the presence of different porosities. OMCs display high surface area, large pore volume, and uniform pore size, which favor mass transport. Therefore, the produced propylene can easily come out of the mesopores, thereby avoiding subsequent cracking and/or hydrogenolysis. Furthermore, the high surface area of OMCs could supply more active sites for the PDH process. In this catalytic reaction, the carboxyl groups are regarded as the active sites. However, no direct quantification and/or theoretical simulation has revealed the actual active sites. Later, Hu et al. [134] synthesized a series of mesoporous carbons with different pore orders and surface properties for PDH. It

Fig. 7. O, N, P, and S groups with armchair and zig-zag terminations on nanocarbon materials.

Fig. 8. (a) Propane conversion and (b) propylene selectivity over different OMCs [133].

was found that the highly ordered mesoporous carbons exhibit higher catalytic activities than disordered and ordered mesoporous carbons, which further reveal that pore ordering plays a crucial role in determining mass transport and the amounts of accessible active sites.

Monolithic mesoporous carbons (COMC) were prepared via an autoclaving method by using citric acid as the catalyst instead of HCl [135]. During this preparation process, citric acid played a key role in determining the channel ordering of the obtained OMCs, because the $-\text{COOH}$ groups in the acid could significantly improve the interactions between F127 template and resorcinol/formaldehyde precursor. After carbonization, COMC with a uniform pore size of ~ 5 nm and a high specific surface area of $758 \text{ m}^2 \text{ g}^{-1}$ would be formed. The resultant COMC was used for PDH, and exhibited high catalytic performance and long-term stability. The initial propane conversion and selectivity of COMC are 22.6% and 89.0%, respectively, which are slightly higher than those of HOMC (prepared by using HCl). This study further illustrates that OMCs prepared by various methods can be used for PDH.

In PDH reaction, the catalytic performances of nanocarbon materials are related to their oxygenated functional groups. Therefore, improvement of the surface oxygenated functional groups is an efficient method to increase the catalytic activities of nanocarbon materials. Through HNO_3 oxidation, the surface functional groups of OMCs can be increased [137]. The resulting HNO_3 -activated OMCs exhibit improved catalytic activity, compared with that of pristine OMCs, for PDH. Inevitably, the activation process also results in many acidic functional groups (such as carboxylic acid groups) on the surface of OMCs, which would lead to deep dehydrogenation and cracking.

Heteroatom-doped OMCs were prepared and used for PDH. Song et al. [138] prepared a series of heteroatom (N, P, and B)-doped OMCs (NMC, PMC, and BMC) for PDH. PMC and BMC exhibited improved catalytic activities, compared with those of undoped OMCs, whereas NMC showed a lower catalytic activity. Characterizations suggest that the amounts of the $\text{C}=\text{O}$ groups of nanocarbons play a key role in PDH. Doping with P and B can increase the number of $\text{C}=\text{O}$ groups in nanocarbons, however, N doping decreases the number of $\text{C}=\text{O}$ groups of nanocarbons. Therefore, the choice of heteroatoms is very important for the preparation of doped nanocarbons for dehydrogenation reactions. Liu and coworkers [139] prepared a series of P-doped CMK-3, which exhibited enhanced catalytic performance in PDH. It was revealed that the $\text{P}=\text{O}$ functional groups are additional possible active sites for PDH. However, no further study was carried out to verify this conclusion.

Although OMCs exhibit high catalytic performances in PDH, their preparation is so complex, time-consuming, and expensive that they are unfavorable for commercial utilization. The development of nanocarbons displaying high catalytic performances (activity, selectivity, and stability) at significantly low costs by using an environmental-friendly method for PDH is very urgent and necessary. Hu et al. [140,141] proposed the utilization of biomass-derived nanocarbons for PDH. Typically, porous carbons with micro/meso/macropores and numerous oxygenated functional groups were prepared by a simple alkali

activation method, in which the castanea mollissima shells were calcined with KOH at a high temperature [140]. During the KOH activation process, many pores would be introduced into the castanea mollissima shell-derived carbons (CMSCs). The CMSCs were used as metal-free catalysts for PDH, and exhibited high activity, selectivity, and stability. It is notable that the calcination temperature and KOH/C ratios corresponding to the activation conditions can significantly affect the catalytic performance of CMSCs. At low calcination temperatures ($<600^\circ\text{C}$), KOH cannot activate the C materials, therefore, only a small number of pores can be introduced into the CMSCs. When the activation temperature is higher than 700°C , a large number of oxygenated functional groups (active sites) of CMSCs would be decomposed, which results in lower catalytic performances. Therefore, 700°C is the suitable activation temperature.

On the basis of the abovementioned studies, it can be concluded that the surface oxygenated functional groups of carbon materials play a key role in PDH. However, there are many kinds of O-containing groups (such as $-\text{OH}$, $-\text{COOH}$, $\text{C}-\text{O}-\text{C}$, and $\text{C}=\text{O}$ groups) in nanocarbon materials. Which kind of functional group is the active site in PDH? Hu et al. [142] developed a sequential oxidation method for the preparation of oxidized MWCNTs. The concentrations and types of the O-containing groups on MWCNTs can be well controlled by sequential acidic oxidation and thermal treatment, as evidenced by TPD-MS and XPS techniques (Fig. 9a–9c). Then, the obtained MWCNTs are used as metal-free catalysts for PDH. It is found that the activities (propylene formation rates) of these nanocarbons show a good linear dependence on the number of carbonyl/quinone groups, which confirms that the $\text{C}=\text{O}$ groups are the active sites (Fig. 9d and 9e). $\text{C}=\text{O}$ groups are basic groups that can activate propane as the electron donor. Then, propylene and hydroxyl groups ($\text{C}-\text{OH}$) would be formed as the target product and intermediate, respectively. The reaction cycle is completed by the thermal decomposition of the $\text{C}-\text{OH}$ groups to molecular H_2 and $\text{C}=\text{O}$ groups.

As metal-free catalysts for PDH, nanocarbons display many advantages such as high stability, non-toxicity, and low cost, which make them a very promising alternative to metal and metal oxide catalysts. The performances of C-based catalysts are strongly affected by their structural and surface properties such as microstructure and surface oxygenated functional groups. The size, shape, and porosity of carbocatalysts can affect the accessibility of the active sites for PDH. The surface oxygenated functional groups, particularly $\text{C}=\text{O}$ groups, are regarded as the active sites in PDH. Therefore, a good C-based PDH catalyst should exhibit a high surface area, be rich in $\text{C}=\text{O}$ groups, and offer high stability. Owing to the high performance of carbocatalysts in PDH, many good results have been obtained in this area. However, the regeneration of deactivated carbocatalysts is a great challenge, owing to the fact that C materials would be burned off in an oxidizing atmosphere.

3.6. Other catalysts

Besides the Pt -, CrO_x -, VO_x -, GaO_x -based catalysts, and nanocarbons, some other metal and/or metal oxides (such as

Fig. 9. TPD-MS curves of (a) oxidized MWCNTs and (b) thermally treated so-MWCNTs. (c) O 1s XPS spectra of raw oxidized MWCNTs. (d) Initial propylene formation rates of oxidized MWCNTs as functions of number of carbonyl groups, calculated from XPS analysis, and (e) TPD-MS results. (f) Schematic illustration of the PDH process on MWCNTs [142].

FeO_x, CoO_x, SnO_x, ZnO_x, and ZrO₂-based catalysts) have been studied as catalysts for PDH reaction, which exhibited comparable and/or higher performances than CrO_x- and Pt-based catalysts.

Supported Fe catalysts have been found to be active for PDH [150–155]. Sun et al. [150] reported that the FeO_x species supported on sulfated alumina was active for PDH. At 560 °C, 20% propylene yield can be obtained over 20Fe/5S-Al catalyst. It is revealed that Fe–O–S is formed in Fe/S-Al catalysts, which results in enhanced acidity and activity. Later, they found that by using Fe²⁺ or Fe³⁺ sulfate as the precursor, pretreating with SO₂, and introducing SO₂ with propane as a reactant can affect the performance of Fe₂O₃/γ-Al₂O₃ catalysts [151]. Particularly, the sulfate species introduced can react with γ-Al₂O₃ support and Fe species (forming Al–O–S and Fe–O–S), which are beneficial for the PDH process. Recently, they reported that pre-reduced Fe₂O₃/Al₂O₃ exhibited a high catalytic performance in PDH [152]. During the pre-reduction process, Fe³⁺ would be transformed into Fe²⁺ and Fe species, which are considered to be the active sites for PDH. However, the catalytic mechanism and active sites of Fe-based catalysts are still unclear. Additionally, Yun et al. [153] prepared a series of Fe-silicate zeolites, namely [Fe]ZSM-5 samples with Si/Fe ratios of 26 and 48, and [Fe]β catalyst with Si/Fe ratio of 15. It was found that the Fe-silicate zeolites exhibited much higher dehydrogenation rates than [Fe]H-[Al]ZSM-5. The redox catalytic cycle suggested that propane radical cations would be formed over the isolated Fe framework sites in [Fe] zeolites during the PDH process. Hu et al. [154] developed a Fe²⁺/SiO₂ catalyst with isolated Fe²⁺ spe-

cies for PDH. By comparing with those of iron oxide particles and metallic nanoparticles on SiO₂, it was found that the isolated Fe²⁺/SiO₂ catalyst exhibits a much higher propylene selectivity. *In situ* XANES results reveal that the active sites involve the Fe²⁺ species. Tan et al. [155] reported that the addition of P could improve the activity of Fe/Al₂O₃ catalyst. Particularly, Fe/P/Al catalysts with Fe:P ratio of 3:1 exhibited the highest activity (propane conversion of 15%, propylene selectivity > 80%). However, their catalytic activities are really low. In particular, the active sites and catalytic mechanisms are still unclear.

Co-based catalysts are reported to be active for PDH [156–160]. Hu et al. [156] reported that single-site Co²⁺ on SiO₂ were active for PDH. Tetrahedrally coordinated Co²⁺ species are highly stabilized on the surface of amorphous silica after pretreatment in H₂ at 650 °C. During the PDH process, this catalyst exhibits high propylene selectivities of over 95% and 90% at the reaction temperatures of 550 and 650 °C, respectively. DFT further indicates that the C–H bond cleavage occurs across a Co–O_{support} bond. Mesoporous CoAl₂O₄ spinel was also prepared for PDH [157]. The resultant Co–Al catalysts exhibit a high propane conversion of 39%, with a propylene selectivity of over 80%. In this catalyst system, the tetrahedral Co²⁺ species is regarded as the active sites, which are Lewis sites and experience no significant change in the coordination environment and oxidation state during the PDH reaction. Furthermore, another metal species was introduced into the Co-based catalysts. Zhao et al. [158] prepared a modified SiO₂ support with isolated Zr atoms for supporting Co²⁺. The as-synthesized

Co-Zr/SiO₂ catalyst exhibited higher activity and selectivity than Co/SiO₂ catalyst, due to a change in the O donating ability and Co–O bond strength of the $\equiv\text{SiO}-\text{Zr}-\text{O}$ sites of Co-Zr/SiO₂. In addition, the states of Co could affect the performance of Co/Al₂O₃ catalyst. After post-treatment of the Co/Al₂O₃ catalysts by using different protocols, they revealed different performances in PDH [159]. Particularly, poor dispersion of Co leads to coking and pyrolysis, while highly dispersed Co species can result in high PDH performances. Furthermore, the addition of sulfate species can affect the performance of Co/Al₂O₃ catalyst in PDH. Sun et al. [160] found that the addition of sulfate could improve the dispersion of Co and restrained the reduction of Co ions to metallic Co species, thereby improving the activity and selectivity of Co-based catalysts. The use of Co-based catalysts for PDH has been rarely reported before. The active sites and catalytic mechanisms are still unclear. Generally, single site and/or isolated Co²⁺ species are regarded as the active sites in PDH. Furthermore, the activity and selectivity are much lower than those of Pt- and CrO_x-based catalysts.

Sn is considered as a promoter for Pt-based catalysts, owing to the formation of Pt–Sn alloy. Wang and coworkers [161,162] reported that Sn supported on SiO₂ exhibited high activity, selectivity and excellent stability in PDH (Fig. 10a–10c). After introduction of a small amount of Pd, the stability of SnPd/SiO₂ catalyst can be enhanced to over 168 h, which is representative of a very promising PDH catalyst. Similarly, Sn-containing hexagonal mesoporous silica (HMS) exhibits a high propane conversion of ~40% and excellent stability over 170 h (Fig. 10d). It is revealed that the high stability of Sn-based catalysts is attributed to the formation of strong Sn–O–Si bonds. However, the active sites and mechanism of Sn-based catalysts have not been understood well. More detailed and theoretical studies on

this kind of catalyst are highly desired.

Supported Zn oxides are also reported to be active for PDH [84–87,163]. Schweitzer et al. [85] developed a strong electrostatic adsorption methodology to synthesize SiO₂-supported single site Zn²⁺ catalysts. It is revealed that the Zn²⁺ are chemisorbed into the strained three-membered siloxane rings present on the amorphous SiO₂ surface. During the PDH reaction, Zn²⁺ loses one Zn–O bond, resulting in a coordinatively unsaturated three-coordinate active center. DFT further reveals that the C–H bonds are activated by a non-redox mechanism. Gong et al. [86] reported that ZnO supported on ZSM-5 and Y zeolites exhibited high catalytic performances in PDH. However, the high acidity of zeolites results in serious cracking and coke formation. Camacho-Bunquin et al. [87] prepared a series of Zn/SiO₂ catalysts by using an integrated atomic layer deposition-catalysis instrument. It is found that the catalytic activity of open shell 16-electron, tri-coordinate ethyl Zn-silica sites is much higher than that of 18-electron, tetra-coordinate ZnO-type centers. Furthermore, the loading amount of Zn can affect the performance of Zn/SiO₂ catalysts. When the SiO₂ surface is saturated with Zn²⁺ sites, a higher Zn loading would result in Zn agglomeration and catalyst deactivation. Very recently, Chen et al. [163] reported that ZnO supported on dealuminated beta zeolite exhibited high catalytic activity and long-term stability. This is ascribed to the zeolite structure, which can provide a special environment for stabilizing Zn species.

Furthermore, ZrO₂ has been studied for the PDH reaction [164–167]. Otroshchenko et al. [164] reported that ZrO₂ promoted with other metal oxides exhibited a high activity for PDH. After addition of 0.05% Cu and La₂O₃ oxides, Cu/ZrO₂–La₂O₃ exhibited industrially relevant activity and durability in PDH. On the other hand, La₂O₃–ZrO₂ and Y₂O₃–ZrO₂

Fig. 10. Catalytic performances of propane dehydrogenation over (a) fresh Sn/SiO₂, (b) regenerated Sn/SiO₂, (c) SnPd/SiO₂, and (d) Sn-HMS catalysts [161,162].

displayed PDH activities that were comparable to that of conventional $\text{K-CrO}_x/\text{Al}_2\text{O}_3$ catalyst [165]. The coordinatively unsaturated Zr cations and neighboring lattice O are responsible for the C–H cleavage occurring during the PDH. Zhang et al. [166] revealed through quantum chemical calculations that ZrO_2 with coordinatively unsaturated Zr sites was active for C–H bond dissociation. Particularly, the crystallite size of ZrO_2 can affect the concentration of anion vacancies in ZrO_2 , and thus, affect the PDH performance.

In summary, the performances of supported transition metal catalysts (such as FeO_x , CoO_x , SnO_x , ZnO_x , and ZrO_2 -based catalysts) in PDH reaction are strongly affected by the preparation methods, type of supports, and nature of active sites. The preparation methods can affect the properties (such as shape, size, and distribution) of the catalysts. The type of supports can affect the stability, states, and electronic properties of the active sites, and thus, affect the catalytic performances. Usually, isolated and/or unsaturated metal species are regarded as the active sites for PDH. However, they exhibit low stability and tend to aggregate into large particles, resulting in low stability and regenerability. Therefore, the development of novel methods and supports for stabilizing these transition metal species is of great significance. Over the last several years, great efforts have been made to improve the stability of transition metal catalysts in PDH. Particularly, surface organometallic method is a very promising method of synthesis of highly stable PDH catalysts with isolated metal active sites [157,159,161]. Owing to the well-defined structure of the metal species, the catalytic mechanisms and active sites of these catalysts can be identified.

4. Summary and outlook

With growing demand for propylene and increasing production of propane from shale gas, direct PDH has drawn particular attention and has been regarded as one of the most promising methods of propylene production. In particular, many new PDH projects have been announced and established in recent years. Up to now, the two widely used crafts are Catofin (CrO_x -based catalysts) and Oleflex (Pt-based catalysts) technologies. These two catalyst systems display many advantages such as high activity and selectivity. However, a few drawbacks (such as cracking, deep dehydrogenation, and coke formation) limit their applications. Over the last several years, great efforts have been made to improve the performances of CrO_x - and Pt-based catalysts by using various strategies, such as using different supports, improving the structural properties, introducing promoters, and/or developing new preparation methods. Although some improvements have been achieved, the stabilities of CrO_x - and Pt-based catalysts are still too low. Therefore, frequent regeneration is required to remove the coke and recover the catalytic activity. For Pt-based catalysts, their stability is slightly higher than that of CrO_x -based catalysts. However, coke formation and sintering of Pt nanoparticles are two key factors affecting the performance of Pt-based catalysts. Recent studies on Pt-based catalysts have focused on the exploitation of single atom Pt and/or Pt-M alloys (where M represents a metal species, such as In, Mn, and Cu) for PDH.

These provide great opportunities for the utilization of Pt species at the atomic scale.

Metal oxides, including VO_x - and GaO_x -based catalysts, are reported to be active for PDH, which represent the most promising alternatives to CrO_x - and Pt-based catalysts. Their catalytic performances are strongly affected by the types of supports, promoters, preparation methods, and loading amounts. VO_x - and GaO_x -based catalysts with high surface areas, suitable acidities, fine dispersions, and moderate metal-supported interactions exhibit high PDH performances. A number of VO_x - and GaO_x -based catalysts have been employed in PDH. However, their performances are still lower than those of CrO_x - and Pt-based catalysts. The development of new efficient methods to improve the stability of VO_x - and GaO_x -based catalysts is still a great challenge. Furthermore, there are many different kinds of V (such as V^{5+} , V^{4+} , V^{3+} , isolated V, oligomeric V^{n+} , and crystalline V_2O_5) and Ga (such as Ga^{3+} , $[\text{GaH}_2]^+$, $[\text{GaH}]^{2+}$, and polymorphs of gallium oxides) species that exist on VO_x - and GaO_x -based catalysts. Revealing the active sites and mechanisms of these catalysts is highly difficult.

Nanocarbons (such as OMCs, biomass-derived porous carbons, and MWCNTs) have also been reported to be active for PDH. Compared with noble metal and metal oxide catalysts, nanocarbons exhibit many advantages, such as high surface area, tunable nanoscale dimension, and abundant functional groups. The structure and surface functional groups can significantly affect their catalytic performance in PDH. In particular, nanocarbons with rich pores and abundant surface functional groups are active for PDH. However, there are many surface functional groups, such as O-containing groups (ketones, carboxylic anhydrides, lactone, carboxylic acid, ether, phenol, etc.), P-containing groups ($-\text{P}=\text{O}$, $-\text{PO}(\text{OH})_2$, $-\text{OPO}(\text{OH})_2$, and $-\text{P}(\text{OH})_2$), N-containing groups (such as pyridine oxide, amide, amine, pyrrole, pyridine, and lactam), and other heteroatoms (B, F, Cl, etc.), in nanocarbons. Revealing the role of each functional group in PDH is extremely difficult. It is reported that defects, C=O, and P=O are responsible for the high catalytic performance of nanocarbons in PDH. However, the catalytic mechanisms of these active sites are still debated. Theoretical calculations and simulations are therefore highly desired.

Additionally, some other supported metal oxides (such as FeO_x , CoO_x , SnO_x , ZnO_x , and ZrO_2 -based catalysts) have been studied for PDH. These have focused on the development of new preparation methods to synthesize alternative catalysts to Pt- and CrO_x -based catalysts. In particular, some novel catalysts with single atoms have been synthesized. Their structural and textural properties, nature of active sites, and catalytic mechanisms have been investigated and identified. In some cases, their catalytic performance is comparable and/or much higher than those of Pt- and CrO_x -based catalysts, which suggests that they are very promising PDH catalysts.

By reviewing the literature, it can be found that isolated and/or single atom catalysts exhibit promising performance in PDH through interaction between the support and the active metal centers, which results in improved stability and anti-coking capability. Even though some work has been carried out on single atom catalysts, more investigations are required

to increase the loading amount and improve the performance of single atom catalysts. Particularly, surface organometallic method has been regarded as one of the most promising methods of synthesis of single atom catalysts. Typically, metal precursors with well-defined structures (metal + organic ligands) are grafted onto supports (such as Al_2O_3 , SiO_2 , and zeolites), which result in single atom and/or double alloy atom catalysts. Owing to the well-defined structure of the active sites, the mechanisms of these catalysts can be easily identified.

Despite significant progress in the past few decades, CrO_x - and Pt-based catalysts are still the most widely used industrial PDH catalysts. These two catalyst systems generally suffer from serious coke formation and low stability. Improving their catalytic performance (including activity, selectivity, and stability) in PDH process is still the main target. Further, more detailed, systematic, and scientific studies on the roles of promoters, interactions between the active sites and supports, acidity of the support, and structural and electronic properties of CrO_x - and Pt-based catalysts are highly desired. Alternatively, a number of metal oxides (VO_x , GaO_x , FeO_x , CoO_x , SnO_x , ZnO_x , and ZrO_x) and nanocarbons (mesoporous C, C nanotubes, and biomass-derived C) have been synthesized and utilized for PDH, which exhibit performances comparable to those of CrO_x - and Pt-based catalysts. Among them, isolated Fe, Co, Sn, Zn, and Zr metals supported on Al_2O_3 , SiO_2 , and zeolites represent highly promising catalysts for PDH. However, the performances (activity, selectivity, and stability) of these catalysts are still unsatisfactory, owing to the low stability and regenerability. Future research should focus on (i) developing new efficient synthesis methods to improve the catalyst stability, (ii) revealing the active sites and catalytic mechanisms, (iii) identifying the interplay between catalyst deactivation and regeneration, and (iv) developing *in situ* and/or operando spectroscopy techniques to monitor the changes occurring in the catalysts (in terms of structure and surface properties) during the PDH

process.

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References

- [1] J. J. H. B. Sattler, J. Ruiz-Martinez, E. Santillan-Jimenez, B. M. Weckhuysen, *Chem. Rev.*, **2014**, 114, 10613–10653.
- [2] M. A. Atanga, F. Rezaei, A. Jawad, M. Fitch, A. A. Rownaghi, *Appl. Catal. B*, **2018**, 220, 429–445.
- [3] Z. J. Zhao, C. C. Chiu, J. Gong, *Chem. Sci.*, **2015**, 6, 4403–4425.
- [4] F. Cavani, N. Ballarini, A. Cericola, *Catal. Today*, **2007**, 127, 113–131.
- [5] L. Liu, Y. P. Zhu, M. Su, Z. Y. Yuan, *ChemCatChem*, **2015**, 7, 2765–2787.
- [6] D. S. Su, S. Perathoner, G. Centi, *Chem. Rev.*, **2013**, 113, 5782–5816.
- [7] W. Qi, P. Yan, D. S. Su, *Acc. Chem. Res.*, **2018**, 51, 640–648.
- [8] Z. Zhao, G. Ge, W. Li, X. Guo, G. Wang, *Chin. J. Catal.*, **2016**, 37, 644–670.
- [9] I. Yarulina, K. De Wispelaere, S. Bailleul, J. Goetze, M. Radersma, E. Abou-Hamad, I. Vollmer, M. Goesten, B. Mezari, E. J. M. Hensen, J. S. Martínez-Espín, M. Morten, S. Mitchell, J. Perez-Ramirez, U. Olsbye, B. M. Weckhuysen, V. V. Speybroeck, F. Kapteijn, J. Gascon, *Nat. Chem.*, **2018**, 10, 804–812.
- [10] J. Zhong, J. Han, Y. Wei, P. Tian, X. Guo, C. Song, Z. Liu, *Catal. Sci. Technol.*, **2017**, 7, 4905–4923.
- [11] P. Munnik, P. E. de Jongh, K. P. de Jong, *J. Am. Chem. Soc.*, **2014**, 136, 7333–7340.
- [12] A. Y. Khodakov, W. Chu, P. Fongarland, *Chem. Rev.*, **2007**, 107, 1692–1744.
- [13] C. J. Weststrate, J. van de Loosdrecht, J. W. Niemantsverdriet, *J.*

Graphical Abstract

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State-of-the-art catalysts for direct dehydrogenation of propane to propylene

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This review presents the state-of-the-art catalysts (including Pt, CrO_x , VO_x , GaO_x , ZnO , FeO_x , CoO_x , SnO_x , ZrO_2 -based catalysts, and nanocarbons) that have been reported in recent years for direct dehydrogenation of propane to propylene.

- Catal.*, **2016**, 342, 1–16.
- [14] L. Shi, Y. Wang, B. Yan, W. Song, D. Shao, A. H. Lu, *Chem. Commun.*, **2018**, 54, 10936–10946.
 - [15] D. Chen, A. Holmen, Z. Sui, X. Zhou, *Chin. J. Catal.*, **2014**, 35, 824–841.
 - [16] I. Kainthla, J. T. Bhanushali, R. S. Keri, B. M. Nagaraja, *Catal. Sci. Technol.*, **2015**, 5, 5062–5076.
 - [17] Z. Nawaz, *Rev. Chem. Eng.*, **2015**, 31, 413–436.
 - [18] J. J. H. B. Sattler, I. D. Gonzalez-Jimenez, A. M. Mens, M. Arias, T. Visser, B. M. Weckhuysen, *Chem. Commun.*, **2013**, 49, 1518–1520.
 - [19] K. Searles, K. W. Chan, J. A. Mendes Burak, D. Zemlyanov, O. Safonova, C. Copéret, *J. Am. Chem. Soc.*, **2018**, 140, 11674–11679.
 - [20] J. Li, J. Li, Z. Zhao, X. Fan, J. Liu, Y. Wei, A. Duan, Z. Xie, Q. Liu, *J. Catal.*, **2017**, 352, 361–370.
 - [21] S. Sokolov, M. Stoyanova, U. Rodemerck, D. Linke, E. V. Kondratenko, *J. Catal.*, **2012**, 293, 67–75.
 - [22] H. Xiong, S. Lin, J. Goetze, P. Pletcher, H. Guo, L. Kovarik, K. Artyushkova, B. M. Weckhuysen, A. K. Datye, *Angew. Chem. Int. Ed.*, **2017**, 56, 8986–8991.
 - [23] J. J. H. B. Sattler, I. D. Gonzalez-Jimenez, L. Luo, B. A. Stears, A. Malek, D. G. Barton, B. A. Kilos, M. P. Kaminsky, T. W. G. M. Verhoeven, E. J. Koers, M. Baldus, B. M. Weckhuysen, *Angew. Chem. Int. Ed.*, **2014**, 53, 9251–9256.
 - [24] J. J. H. B. Sattler, A. M. Mens, B. M. Weckhuysen, *ChemCatChem*, **2014**, 6, 3139–3145.
 - [25] J. McGregor, Z. Huang, E. P. Parrott, J. A. Zeitler, K. L. Nguyen, J. M. Rawson, A. Carley, T. W. Hansen, J. P. Tessonnier, D. S. Su, D. Teschner, E. M. Vass, A. Knop-Gericke, R. Schlögl, L. F. Gladden, *J. Catal.*, **2010**, 269, 329–339.
 - [26] Z. Lian, S. Ali, T. Liu, C. Si, B. Li, D. S. Su, *ACS Catal.*, **2018**, 8, 4694–4704.
 - [27] S. M. Airaksinen, M. A. Bañares, A. O. I. Krause, *J. Catal.*, **2005**, 230, 507–513.
 - [28] F. E. Frey, W. F. Huppke, *Ind. Eng. Chem.*, **1933**, 25, 54–59.
 - [29] W. Z. Lang, C. L. Hu, L. F. Chu, Y. J. Guo, *RSC Adv.*, **2014**, 4, 37107–37113.
 - [30] A. Węgrzyniak, S. Jarczewski, A. Węgrzynowicz, B. Michorczyk, P. Kuśtrowski, P. Michorczyk, *Nanomaterials*, **2017**, 7, 249.
 - [31] M. S. Kumar, N. Hammer, M. Rønning, A. Holmen, D. Chen, J. C. Walmsley, G. Øye, *J. Catal.*, **2009**, 261, 116–128.
 - [32] V. Z. Fridman, R. Xing, M. Severance, *Appl. Catal. A*, **2016**, 523, 39–53.
 - [33] J. Baek, H. J. Yun, D. Yun, Y. Choi, J. Yi, *ACS Catal.*, **2012**, 2, 1893–1903.
 - [34] T. P. Otroshchenko, U. Rodemerck, D. Linke, E. V. Kondratenko, *J. Catal.*, **2017**, 356, 197–205.
 - [35] A. Węgrzyniak, S. Jarczewski, A. Wach, E. Hędrzak, P. Kuśtrowski, P. Michorczyk, *Appl. Catal. A*, **2015**, 508, 1–9.
 - [36] C. Copéret, D. P. Estes, K. Larmier, K. Searles, *Chem. Rev.*, **2016**, 116, 8463–8505.
 - [37] C. Copéret, F. Allouche, K. W. Chan, M. P. Conley, M. F. Delley, A. Fedorov, I. B. Moroz, V. Mougél, M. Pucino, K. Searles, K. Yamamoto, P. A. Zhizhko, *Angew. Chem. Int. Ed.*, **2018**, 57, 6398–6440.
 - [38] M. P. Conley, M. F. Delley, F. Núñez-Zarur, A. Comas-Vives, C. Copéret, *Inorg. Chem.*, **2015**, 54, 5065–5078.
 - [39] M. F. Delley, M. C. Silaghi, F. Núñez-Zarur, K. V. Kovtunov, O. G. Salnikov, D. P. Estes, I. V. Koptuyug, C. Copéret, *Organometallics*, **2016**, 36, 234–244.
 - [40] M. G. Cutrufello, S. De Rossi, I. Ferino, R. Monaci, E. Rombi, V. Solinas, *Thermochim. Acta*, **2005**, 434, 62–68.
 - [41] A. Węgrzyniak, A. Rokicińska, E. Hędrzak, B. Michorczyk, K. Zeńczak-Tomera, P. Kuśtrowski, P. Michorczyk, *Catal. Sci. Technol.*, **2017**, 7, 6059–6068.
 - [42] T. H. Kim, M. Y. Gim, J. H. Song, W. C. Choi, Y. K. Park, U. G. Hong, D. S. Park, I. K. Song, *Catal. Commun.*, **2017**, 97, 37–41.
 - [43] S. Sim, S. Gong, J. Bae, Y. K. Park, J. Kim, W. C. Choi, D. S. Hong, I. K. Song, H. Seo, N. Y. Kang, S. Park, *Mol. Catal.*, **2017**, 436, 164–173.
 - [44] F. Cabrera, D. Ardisson, O. F. Gorris, *Catal. Today*, **2008**, 133–135, 800–804.
 - [45] P. P. Li, W. Z. Lang, K. Xia, L. Luan, X. Yan, Y. J. Guo, *Appl. Catal. A*, **2016**, 522, 172–179.
 - [46] K. H. Kang, T. H. Kim, W. C. Choi, Y. K. Park, U. G. Hong, D. S. Park, C. J. Kim, I. K. Song, *Catal. Commun.*, **2015**, 72, 68–72.
 - [47] S. A. Dzhamalova, *Russ. J. Appl. Chem.*, **2010**, 83, 2152–2157.
 - [48] R. P. Dzhabarov, S. M. Gadzhizade, S. A. Dzhamalova, N. A. Aliev, A. A. Kasimov, *Kinet. Catal.*, **2012**, 53, 280–285.
 - [49] Q. Li, Z. Sui, X. Zhou, Y. Zhu, J. Zhou, D. Chen, *Top. Catal.*, **2011**, 54, 888–896.
 - [50] Y. L. Shan, T. Wang, Z. J. Sui, Y. A. Zhu, X. G. Zhou, *Catal. Commun.*, **2016**, 84, 85–88.
 - [51] Y. L. Shan, Y. A. Zhu, Z. J. Sui, D. Chen, X. G. Zhou, *Catal. Sci. Technol.*, **2015**, 5, 3991–4000.
 - [52] J. Zhu, M. L. Yang, Y. Yu, Y. A. Zhu, Z. J. Sui, X. G. Zhou, A. Holmen, D. Chen, *ACS Catal.*, **2015**, 5, 6310–6319.
 - [53] S. Saerens, M. K. Sabbe, V. V. Galvita, E. A. Redekop, M. F. Reyniers, G. B. Marin, *ACS Catal.*, **2017**, 7, 7495–7508.
 - [54] Y. Zhang, Y. Zhou, J. Shi, S. Zhou, X. Sheng, Z. Zhang, S. Xiang, *J. Mol. Catal. A*, **2014**, 381, 138–147.
 - [55] L. Shi, G. M. Deng, W. C. Li, S. Miao, Q. N. Wang, W. P. Zhang, A. H. Lu, *Angew. Chem. Int. Ed.*, **2015**, 54, 13994–13998.
 - [56] F. T. Zangeneh, S. Mehrzama, S. Sahebdehfar, *Fuel Process. Technol.*, **2013**, 109, 118–123.
 - [57] C. Sun, J. Luo, M. Cao, P. Zheng, G. Li, J. Bu, Z. Gao, S. Chen, X. Xie, *J. Energy Chem.*, **2018**, 27, 311–318.
 - [58] F. Jiang, L. Zeng, S. Li, G. Liu, S. Wang, J. Gong, *ACS Catal.*, **2014**, 5, 438–447.
 - [59] G. Siddiqi, P. Sun, V. Galvita, A. T. Bell, *J. Catal.*, **2010**, 274, 200–206.
 - [60] O. B. Belskaya, L. N. Stepanova, T. I. Gulyaeva, S. B. Erenburg, S. V. Trubina, K. Kvashnina, A. I. Nizovskii, A. V. Kalinkin, V. I. Zaikovskii, V. I. Bukhtiyarov, V. A. Likhobolov, *J. Catal.*, **2016**, 341, 13–23.
 - [61] M. Filez, E. A. Redekop, H. Poelman, V. V. Galvita, M. Meledina, S. Turner, G. V. Tendeloo, C. Detavernier, G. B. Marin, *Catal. Sci. Technol.*, **2016**, 6, 1863–1869.
 - [62] K. Xia, W. Z. Lang, P. P. Li, L. L. Long, X. Yan, Y. J. Guo, *Chem. Eng. J.*, **2016**, 284, 1068–1079.
 - [63] T. Wang, F. Jiang, G. Liu, L. Zeng, Z. J. Zhao, J. Gong, *AIChE J.*, **2016**, 62, 4365–4376.
 - [64] L. L. Long, K. Xia, W. Z. Lang, L. L. Shen, Q. Yang, X. Yan, Y. J. Guo, *J. Ind. Eng. Chem.*, **2017**, 51, 271–280.
 - [65] L. Huang, B. Xu, L. Yang, Y. Fan, *Catal. Commun.*, **2008**, 9, 2593–2597.
 - [66] X. Fan, J. Li, Z. Zhao, Y. Wei, J. Liu, A. Duan, G. Jiang, *Catal. Sci. Technol.*, **2015**, 5, 339–350.
 - [67] Z. Nawaz, X. Tang, Y. Chu, F. Wei, *Chin. J. Catal.*, **2010**, 31, 552–556.
 - [68] Y. Zhang, Y. Zhou, L. Huang, S. Zhou, X. Sheng, Q. Wang, C. Zhang, *Chem. Eng. J.*, **2015**, 270, 352–361.
 - [69] A. Volynkin, M. Rønning, E. A. Blekkan, *Top. Catal.*, **2015**, 58, 854–865.
 - [70] J. Liu, Y. Yue, H. Liu, Z. Da, C. Liu, A. Ma, J. Rong, D. Su, X. Bao, H. Zheng, *ACS Catal.*, **2017**, 7, 3349–3355.
 - [71] J. Liu, J. Li, J. Rong, C. Liu, Z. Dai, J. Bao, Z. Da, H. Zheng, *Appl. Surf. Sci.*, **2019**, 464, 146–152.
 - [72] A. Iglesias-Juez, A. M. Beale, K. Maaijen, T. C. Weng, P. Glatzel, B. M.

- Weckhuysen, *J. Catal.*, **2010**, 276, 268–279.
- [73] L. Nykänen, K. Honkala, *ACS Catal.*, **2013**, 3, 3026–3030.
- [74] H. Zhu, D. H. Anjum, Q. Wang, E. Abou-Hamad, L. Emsley, H. Dong, P. Laveille, L. Li, A. K. Samal, J. M. Basset, *J. Catal.*, **2014**, 320, 52–62.
- [75] Y. Zhu, Z. An, H. Song, X. Xiang, W. Yan, J. He, *ACS Catal.*, **2017**, 7, 6973–6978.
- [76] F. T. Zangeneh, A. Taeb, K. Gholivand, S. Sahebdehfar, *Appl. Surf. Sci.*, **2015**, 357, 172–178.
- [77] B. Li, Z. Xu, W. Chu, S. Luo, F. Jing, *Chin. J. Catal.*, **2017**, 38, 726–735.
- [78] H. Zhou, J. Gong, B. Xu, L. Yu, Y. Fan, *Appl. Catal. A*, **2016**, 527, 30–35.
- [79] H. Zhou, J. Gong, B. Xu, S. Deng, Y. Ding, L. Yu, Y. Fan, *Chin. J. Catal.*, **2017**, 38, 529–536.
- [80] L. Deng, H. Miura, T. Shishido, Z. Wang, S. Hosokawa, K. Teramura, T. Tanaka, *J. Catal.*, **2018**, 365, 277–291.
- [81] J. Camacho-Bunquin, M. S. Ferrandon, H. Sohn, A. J. Kropf, C. Yang, J. Wen, R. A. Hackler, C. Liu, G. Celik, C. L. Marshall, P. C. Stair, M. Delferro, *ACS Catal.*, **2018**, 8, 10058–10063.
- [82] V. J. Cybulskis, B. C. Bukowski, H. T. Tseng, J. R. Gallagher, Z. Wu, E. Wegener, A. J. Kropf, B. Ravel, F. H. Ribeiro, J. Greeley, J. T. Miller, *ACS Catal.*, **2017**, 7, 4173–4181.
- [83] C. Chen, M. Sun, Z. Hu, J. Ren, S. Zhang, Z. Y. Yuan, *Catal. Sci. Technol.*, **2019**, DOI: 10.1039/c9cy00237e.
- [84] G. Liu, L. Zeng, Z. J. Zhao, H. Tian, T. Wu, J. Gong, *ACS Catal.*, **2016**, 6, 2158–2162.
- [85] N. M. Schweitzer, B. Hu, U. Das, H. Kim, J. Greeley, L. A. Curtiss, P. C. Stair, J. T. Miller, A. S. Hock, *ACS Catal.*, **2014**, 4, 1091–1098.
- [86] T. Gong, L. Qin, J. Lu, H. Feng, *Phys. Chem. Chem. Phys.*, **2016**, 18, 601–614.
- [87] J. Camacho-Bunquin, P. Aich, M. Ferrandon, U. Das, A. Getsoian, U. Das, F. Dogan, L. A. Curtiss, J. T. Miller, C. L. Marshall, A. S. Hock, P. C. Stair, *J. Catal.*, **2017**, 345, 170–182.
- [88] S. Zha, G. Sun, T. Wu, J. Zhao, Z. J. Zhao, J. Gong, *Chem. Sci.*, **2018**, 9, 3925–3931.
- [89] P. Sun, G. Siddiqi, W. C. Vining, M. Chi, A. T. Bell, *J. Catal.*, **2011**, 282, 165–174.
- [90] X. Liu, W. Z. Lang, L. L. Long, C. L. Hu, L. F. Chu, Y. J. Guo, *Chem. Eng. J.*, **2014**, 247, 183–192.
- [91] L. L. Shen, K. Xia, W. Z. Lang, L. F. Chu, X. Yan, Y. J. Guo, *Chem. Eng. J.*, **2017**, 324, 336–346.
- [92] G. Sun, Z. J. Zhao, R. Mu, S. Zha, L. Li, S. Chen, K. Zang, J. Luo, Z. Li, S. C. Purdy, A. J. Kropf, J. T. Miller, L. Zeng, J. Gong, *Nat. Commun.*, **2018**, 9, 4454.
- [93] W. Cai, R. Mu, S. Zha, G. Sun, S. Chen, Z. J. Zhao, H. Li, H. Tian, Y. Tang, F. Tao, L. Zeng, L. Gong, *Sci. Adv.*, **2018**, 4, eaar5418.
- [94] Z. Wu, B. C. Bukowski, Z. Li, C. Milligan, L. Zhou, T. Ma, Y. Wu, Y. Ren, F. H. Ribeiro, W. N. Delgass, J. Greeley, G. Zhang, J. T. Miller, *J. Am. Chem. Soc.*, **2018**, 140, 14870–14877.
- [95] G. Q. Ren, G. X. Pei, Y. J. Ren, K. P. Liu, Z. Q. Chen, J. Y. Yang, Y. Su, X. Y. Liu, W. Z. Li, T. Zhang, *J. Catal.*, **2018**, 366, 115–126.
- [96] R. R. Langeslay, D. M. Kaphan, C. L. Marshall, P. C. Stair, A. P. Sattelberger, M. Delferro, *Chem. Rev.*, **2019**, 119, 2128–2191.
- [97] S. Sokolov, M. Stoyanova, U. Rodemerck, D. Linke, E. V. Kondratenko, *Catal. Sci. Technol.*, **2014**, 4, 1323–1332.
- [98] S. Sokolov, V. Y. Bychkov, M. Stoyanova, U. Rodemerck, U. Benstrup, D. Linke, Y. P. Tyulenin, V. N. Korchak, E. V. Kondratenko, *ChemCatChem*, **2015**, 7, 1691–1700.
- [99] G. Liu, Z. J. Zhao, T. Wu, L. Zeng, J. Gong, *ACS Catal.*, **2016**, 6, 5207–5214.
- [100] P. Hu, W. Z. Lang, X. Yan, L. F. Chu, Y. J. Guo, *J. Catal.*, **2018**, 358, 108–117.
- [101] P. Bai, Z. Ma, T. Li, Y. Tian, Z. Zhang, Z. Zhong, W. Xing, P. Wu, X. Liu, Z. Yan, *ACS Appl. Mater. Interfaces*, **2016**, 8, 25979–25990.
- [102] U. Rodemerck, M. Stoyanova, E. V. Kondratenko, D. Linke, *J. Catal.*, **2017**, 352, 256–263.
- [103] T. Wu, G. Liu, L. Zeng, G. Sun, S. Chen, R. Mu, S. A. Gbonfoun, Z. J. Zhao, J. Gong, *AIChE J.*, **2017**, 63, 4911–4919.
- [104] Z. J. Zhao, T. Wu, C. Xiong, G. Sun, R. Mu, L. Zeng, J. Gong, *Angew. Chem. Int. Ed.*, **2018**, 57, 6791–6795.
- [105] B. Zheng, W. Hua, Y. Yue, Z. Gao, *J. Catal.*, **2005**, 232, 143–151.
- [106] C. T. Shao, W. Z. Lang, X. Yan, Y. J. Guo, *RSC Adv.*, **2017**, 7, 4710–4723.
- [107] M. Chen, J. Xu, F. Z. Su, Y. M. Liu, Y. Cao, H. Y. He, K. N. Fan, *J. Catal.*, **2008**, 256, 293–300.
- [108] K. Searles, G. Siddiqi, O. V. Safonova, C. Copéret, *Chem. Sci.*, **2017**, 8, 2661–2666.
- [109] K. C. Szeto, Z. R. Jones, N. Merle, C. Rios, A. Gallo, F. Le Quemener, L. Delevoye, R. M. Gauvin, S. L. Scott, M. Taoufik, *ACS Catal.*, **2018**, 8, 7566–7577.
- [110] Y. Ren, J. Wang, W. Hua, Y. Yue, Z. Gao, *J. Ind. Eng. Chem.*, **2012**, 18, 731–736.
- [111] W. G. Kim, J. So, S. W. Choi, Y. Liu, R. S. Dixit, C. Sievers, D. S. Sholl, S. Nair, C. W. Jones, *Chem. Mater.*, **2017**, 29, 7213–7222.
- [112] S. W. Choi, W. G. Kim, J. S. So, J. S. Moore, Y. Liu, R. S. Dixit, J. G. Pendergast, C. Sievers, D. S. Sholl, S. Nair, C. W. Jones, *J. Catal.*, **2017**, 345, 113–123.
- [113] M. W. Schreiber, C. P. Plaisance, M. Baumgärtl, K. Reuter, A. Jentys, R. Bermejo-Deval, J. A. Lercher, *J. Am. Chem. Soc.*, **2018**, 140, 4849–4859.
- [114] E. Mansoor, M. Head-Gordon, A. T. Bell, *ACS Catal.*, **2018**, 8, 6146–6162.
- [115] N. Phadke, J. Van der Mynsbrugge, E. Mansoor, A. Getsoian, M. Head-Gordon, A. T. Bell, *ACS Catal.*, **2018**, 8, 6106–6126.
- [116] S. Tan, L. B. Gil, N. Subramanian, D. S. Sholl, S. Nair, C. W. Jones, J. S. Moore, Y. Liu, R. S. Dixit, J. G. Pendergast, *Appl. Catal. A*, **2015**, 498, 167–175.
- [117] S. Tan, S. J. Kim, J. S. Moore, Y. Liu, R. S. Dixit, J. G. Pendergast, D. S. Sholl, S. Nair, C. W. Jones, *ChemCatChem*, **2016**, 8, 214–221.
- [118] X. X. Hou, Q. F. Deng, T. Z. Ren, Z. Y. Yuan, *Environ. Sci. Pollut. Res.*, **2013**, 20, 8521–8534.
- [119] L. Liu, Q. F. Deng, T. Y. Ma, X. Z. Lin, X. X. Hou, Y. P. Liu, Z. Y. Yuan, *J. Mater. Chem.*, **2011**, 21, 16001–16009.
- [120] L. Liu, Q. F. Deng, X. X. Hou, Z. Y. Yuan, *J. Mater. Chem.*, **2012**, 22, 15540–15548.
- [121] J. T. Ren, G. G. Yuan, C. C. Weng, L. Chen, Z. Y. Yuan, *ChemCatChem*, **2018**, 10, 1–10.
- [122] J. T. Ren, Z. Y. Yuan, *ChemCatChem*, **2018**, 10, 3260–3268.
- [123] M. H. Sun, S. Z. Huang, L. H. Chen, Y. Li, X. Y. Yang, Z. Y. Yuan, B. L. Su, *Chem. Soc. Rev.*, **2016**, 45, 3479–3563.
- [124] T. Y. Ma, L. Liu, Z. Y. Yuan, *Chem. Soc. Rev.*, **2013**, 42, 3977–4003.
- [125] J. T. Ren, G. G. Yuan, C. C. Weng, Z. Y. Yuan, *Electrochim. Acta*, **2018**, 261, 454–463.
- [126] J. T. Ren, Y. J. Song, Z. Y. Yuan, *J. Energy Chem.*, **2019**, 32, 78–84.
- [127] J. T. Ren, L. Chen, C. C. Weng, G. G. Yuan, Z. Y. Yuan, *ACS Appl. Mater. Interfaces*, **2018**, 10, 33276–33286.
- [128] J. T. Ren, G. G. Yuan, C. C. Weng, Z. Y. Yuan, *ACS Sustainable Chem. Eng.*, **2017**, 6, 707–718.
- [129] H. Li, Y. Sun, Z. Y. Yuan, Y. P. Zhu, T. Y. Ma, *Angew. Chem. Int. Ed.*, **2018**, 57, 3222–3227.
- [130] Y. P. Zhu, T. Y. Ma, T. Z. Ren, J. Li, G. H. Du, Z. Y. Yuan, *Appl. Catal. B*, **2014**, 156–157, 44–52.
- [131] M. Chen, L. L. Shao, X. Qian, T. Z. Ren, Z. Y. Yuan, *J. Mater. Chem. C*,

- 2014**, 2, 10312–10321.
- [132] M. Chen, L. L. Shao, Z. M. Gao, T. Z. Ren, Z. Y. Yuan, *J. Power Sources*, **2015**, 286, 82–90.
- [133] L. Liu, Q. F. Deng, B. Agula, X. Zhao, T. Z. Ren, Z. Y. Yuan, *Chem. Commun.*, **2011**, 47, 8334–8336.
- [134] Z. P. Hu, J. T. Ren, D. Yang, Z. Wang, Z. Y. Yuan, *Chin. J. Catal.*, **2019**, DOI: S1872-2067(19)63334-6.
- [135] L. Liu, Q. F. Deng, B. Agula, T. Z. Ren, Y. P. Liu, B. Zhaorigetu, Z. Y. Yuan, *Catal. Today*, **2012**, 186, 35–41.
- [136] R. Wang, X. Sun, B. Zhang, X. Sun, D. Su, *Chem. Eur. J.*, **2014**, 20, 6324–6331.
- [137] L. Liu, Q. F. Deng, Y. P. Liu, T. Z. Ren, Z. Y. Yuan, *Catal. Commun.*, **2011**, 16, 81–85.
- [138] Y. Song, G. Liu, Z. Y. Yuan, *RSC Adv.*, **2016**, 6, 94636–94642.
- [139] L. Li, W. Zhu, Y. Liu, L. Shi, H. Liu, Y. Ni, S. Liu, H. Zhou, Z. Liu, *RSC Adv.*, **2015**, 5, 56304–56310.
- [140] Z. P. Hu, H. Zhao, C. Chen, Z. Y. Yuan, *Catal. Today*, **2018**, 316, 214–222.
- [141] Z. P. Hu, L. F. Zhang, Z. Wang, Z. Y. Yuan, *J. Chem. Technol. Bio-technol.*, **2018**, 93, 3410–3417.
- [142] Z. P. Hu, C. Chen, J. T. Ren, Z. Y. Yuan, *Appl. Catal. A*, **2018**, 559, 85–93.
- [143] J. L. Figueiredo, M. F. R. Pereira, *Catal. Today*, **2010**, 150, 2–7.
- [144] J. Deng, M. Li, Y. Wang, *Green Chem.*, **2016**, 18, 4824–4854.
- [145] X. Sun, Y. Ding, B. Zhang, R. Huang, D. Chen, D. S. Su, *ACS Catal.*, **2015**, 5, 2436–2444.
- [146] I. Gerber, M. Oubenali, R. Bacsá, J. Durand, A. Gonçalves, M. F. R. Pereira, F. Jolibois, L. Perrin, R. Poteau, P. Serp, *Chem. Eur. J.*, **2011**, 17, 11467–11477.
- [147] Y. P. Zhu, Y. Liu, Y. P. Liu, T. Z. Ren, T. Chen, Z. Y. Yuan, *ChemCatChem*, **2015**, 7, 2903–2909.
- [148] Y. P. Zhu, Y. Liu, Y. P. Liu, T. Z. Ren, G. H. Du, T. Chen, Z. Y. Yuan, *J. Mater. Chem. A*, **2015**, 3, 11725–11729.
- [149] Y. P. Zhu, Y. P. Liu, Z. Y. Yuan, *Chem. Commun.*, **2016**, 52, 2118–2121.
- [150] Y. N. Sun, L. Tao, T. You, C. Li, H. Shan, *Chem. Eng. J.*, **2014**, 244, 145–151.
- [151] Y. Sun, Y. Wu, H. Shan, G. Wang, C. Li, *Catal. Sci. Technol.*, **2015**, 5, 1290–1298.
- [152] Y. Sun, Y. Wu, L. Tao, H. Shan, G. Wang, C. Li, *J. Mol. Catal. A*, **2015**, 397, 120–126.
- [153] J. H. Yun, R. F. Lobo, *J. Catal.*, **2014**, 312, 263–270.
- [154] B. Hu, N. M. Schweitzer, G. Zhang, S. J. Kraft, D. J. Childers, M. P. Lanci, J. T. Miller, A. S. Hock, *ACS Catal.*, **2015**, 5, 3494–3503.
- [155] S. Tan, B. Hu, W. G. Kim, S. H. Pang, J. S. Moore, Y. Liu, R. S. Dixit, J. G. Pendergast, D. S. Sholl, S. Nair, C. W. Jones, *ACS Catal.*, **2016**, 6, 5673–5683.
- [156] B. Hu, N. M. Schweitzer, U. Das, H. Kim, J. Niklas, O. Poluektov, L. A. Curtiss, P. C. Stair, J. T. Miller, A. S. Hock, *J. Catal.*, **2015**, 322, 24–37.
- [157] B. Hu, W. G. Kim, T. P. Sulmonetti, M. L. Sarazen, S. Tan, J. So, Y. Liu, R. S. Dixit, S. Nair, C. W. Jones, *ChemCatChem*, **2017**, 9, 3330–3337.
- [158] Y. Zhao, H. Sohn, B. Hu, J. Niklas, O. G. Poluektov, J. Tian, M. Delferro, A. S. Hock, *ACS Omega*, **2018**, 3, 11117–11127.
- [159] X. Li, P. Wang, H. Wang, C. Li, *Appl. Surf. Sci.*, **2018**, 441, 688–693.
- [160] Y. N. Sun, Y. N. Gao, Y. Wu, H. Shan, G. Wang, C. Li, *Catal. Commun.*, **2015**, 60, 42–45.
- [161] G. Wang, H. Zhang, H. Wang, Q. Zhu, C. Li, H. Shan, *J. Catal.*, **2016**, 344, 606–608.
- [162] G. Wang, H. Zhang, Q. Zhu, X. Zhu, X. Li, H. Wang, C. Li, H. Shan, *J. Catal.*, **2017**, 351, 90–94.
- [163] C. Chen, Z. Hu, J. Ren, S. Zhang, Z. Wang, Z. Y. Yuan, *ChemCatChem*, **2019**, 11, 868–877.
- [164] T. Otroshchenko, S. Sokolov, M. Stoyanova, V. A. Kondratenko, U. Rodemerck, D. Linke, E. V. Kondratenko, *Angew. Chem. Int. Ed.*, **2015**, 54, 15880–15883.
- [165] T. Otroshchenko, V. A. Kondratenko, U. Rodemerck, D. Linke, E. V. Kondratenko, *J. Catal.*, **2017**, 348, 282–290.
- [166] Y. Zhang, Y. Zhao, T. Otroshchenko, H. Lund, M. M. Pohl, U. Rodemerck, D. Linke, H. Jiao, G. Jiang, E. V. Kondratenko, *Nat. Commun.*, **2018**, 9, 3794.
- [167] T. P. Otroshchenko, V. A. Kondratenko, U. Rodemerck, D. Linke, E. V. Kondratenko, *Catal. Sci. Technol.*, **2017**, 7, 4499–4510.

丙烷直接脱氢催化剂的研究进展

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摘要: 丙烯是一种重要化工原料, 可以用于生产聚丙烯、丙烯腈、丙烯酸、甘油及异丙醇等化学品。近年来, 随着丙烯下游产品需求量的增加, 传统丙烯生产技术(石油催化裂解、石脑油催化裂化)难以满足日益增长的丙烯需求, 寻求新的丙烯生产技术成为石油化工行业的重要趋势。另外, 由于美国页岩气开采技术日益成熟, 大量廉价的丙烷被开采出来。丙烷直接脱氢制丙烯成本大大降低, 并逐渐成为丙烯生产来源的一个重要方面。丙烷脱氢工艺中最重要的就是催化剂的制备和研究, 常见的丙烷脱氢催化剂为CrO_x基催化剂和Pt基催化剂体系, 并被广泛应用于工业丙烷脱氢体系。但是, Cr基催化剂积碳严重, 需要反复再生; 而Pt基催化剂价格昂贵, 且Pt颗粒容易发生团聚而发生不可逆失活。因此, 提高现有CrO_x基和Pt基催化剂的稳定性或开发新型替代型丙烷脱氢催化剂成为提高丙烷脱氢工艺的关键。

本文综述了近年来丙烷直接脱氢制丙烯催化剂的研究进展, 详细讨论了不同催化剂(包括Pt, CrO_x, VO_x, GaO_x, ZnO, FeO_x, CoO_x, SnO_x, ZrO₂基催化剂和碳基催化剂)的活性位点、催化机理及助剂类型和载体种类等对催化剂性能的影响。研究表明, 丙烷脱氢催化剂的催化性能与活性物种的分散性和催化剂酸性关系很大。一般而言, 活性物种分散性越高, 催化剂的催化性能越好。而酸性过高会影响丙烯的脱附过程, 因而会导致丙烷的深度脱氢、裂解或积碳的形成。因此, 提高活性位的分散性和调节催化剂酸性是目前丙烷脱氢催化剂研究的重要方面。最近的一些研究主要集中在制备单分散(单原子)或双原子合金催化剂用于丙烷脱氢, 大大提高催化剂的稳定性。

目前, CrO_x 基和Pt基催化剂仍是丙烷脱氢反应的主要催化剂, 提高它们的活性、稳定性、选择性和抗积碳能力仍是丙烷脱氢工艺研究的重要方面. 另外, 一些新型负载型金属氧化物(如 VO_x , GaO_x , FeO_x , CoO_x , SnO_x , ZnO_x , ZrO_x)和纳米碳材料(介孔碳、碳纳米管和生物质碳)被发现是良好的丙烷脱氢催化剂. 但是, 这些催化剂也面临失活严重和循环性差等问题. 因此, 未来的研究目标需要集中在以下几方面: (1)开发新型制备工艺, 提高催化剂稳定性; (2)明确催化剂活性位点、催化机理和构效关系; (3)明确催化剂失活和再生循环机制; (4)发展原位或operando技术监测丙烷脱氢催化剂的实时变化情况.

关键词: 丙烷脱氢; 丙烯; 非均相催化剂; 活性位; 催化机理

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