



## CRITICAL REVIEW

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# Direct and oxidative dehydrogenation of propane: from catalyst design to industrial application

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The direct formation of propene from propane is a well-established commercial process, which on the basis of energy consumption, is environmentally preferred to the current large-scale sources of propene from steam cracking and fluid catalytic cracking. Propene is a major platform chemical with applications in the polymer and chemical industry and its place in modern society is guaranteed over the coming decades. At present, sources of propane are mostly non-renewable, but the development of technologies to produce renewable "green" propane are gaining traction, which coupled with new catalytic processes will provide the platform to produce green propene. In this critical review, we examine the significant advances made in the development of dehydrogenation catalysts, evaluating the technological and environmental merits. Currently, non-oxidative direct dehydrogenation (DDH) is the only commercialised process, and this is reflected in the high space-time yield commonly reported over the most active catalysts which are typically Pt or Cr based. However, the formation of coke over even the most selective catalysts necessitates multi-reactor cycling to facilitate regeneration. Oxidative dehydrogenation using O<sub>2</sub> (ODH-O<sub>2</sub>) does not suffer from coke formation, but can lead to overoxidation, limiting the yield of propene. While no commercial processes have yet been developed, a promising new class of ODH-O<sub>2</sub> catalysts has emerged in recent years which use boron as the active component. These catalysts are amongst the most active and selective reported to date for this reaction. The use of CO<sub>2</sub> as a soft oxidant (ODH-CO<sub>2</sub>) has also gained interest due to the environmental advantages of utilising CO<sub>2</sub>. Although this is an attractive prospect with considerable potential, the propene yields reported over these catalysts are an order of magnitude lower than the most active DDH and ODH-O<sub>2</sub> catalysts. Despite significant advances in the past decade, current ODH-CO<sub>2</sub> catalysts remain far from displaying the activity levels necessary to be considered for commercial application. The specific requirements of catalyst design for each sub-reaction are discussed and we identify that, regardless of the method of dehydrogenation, the balance of acid and base sites on the catalyst surface is of paramount importance. Future catalyst design in DDH and ODH-O<sub>2</sub> should focus on improving selectivity to propene, while ODH-CO<sub>2</sub> catalysts are limited by their low intrinsic activity with respect to CO<sub>2</sub>. The scarcity of some common catalytic elements is also discussed, with recommendations focusing on more abundant chemical elements. Future research should focus on the low temperature activation of CO<sub>2</sub> as a priority. With further research and development of lower energy routes to propene based on the dehydrogenation of green propane, it should be possible to transform the manufacturing landscape of this key chemical intermediate.

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## 1. Introduction

### 1.1. The importance of propene in modern society

Propene is a major platform chemical with a myriad of uses in the manufacturing and chemical industry. The majority of propene is used to manufacture polypropylene, a recyclable thermoplastic polymer which is second only to polyethylene in the scale of production. Polypropylene has favourable physical properties such as high chemical resistance and good elasticity, which makes it useful in a broad range of applications, includ-

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ing packaging, manufacturing and in construction materials. Propene is also the precursor to many other polymer-related chemicals, including propene oxide (used to make polyurethane), acrylic acid (used to make acrylic polymers) and acrylonitrile (used to make polypropenenitrile). Additionally, large scale chemicals such as isopropanol and cumene (used to manufacture phenol and acetone) are made from propene. Annual propene production was around 130 megatonnes in 2019<sup>1</sup> and is predicted to increase to 191 megatonnes by 2030. Significantly, the expected growth in propane demand cannot be met by existing processes, which are based on steam-cracking (SC) and fluid catalytic cracking (FCC). Instead, direct or on-purpose processes are being developed to fill the so-called 'propene gap'. The focus of this critical review is on the dehydrogenation of propane.

Direct dehydrogenation can be performed either with or without an oxidant present, and O<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>O can all participate as oxidants to form propene from propane. The discovery of active and selective catalysts is central to the development of these on-purpose technologies and is the focus of the current review. Research into propane dehydrogenation is an ever-growing field and to date there are several review articles available on direct dehydrogenation (DDH) (Sattler,<sup>2</sup> 2013), soft oxidation with CO<sub>2</sub> (ODH-CO<sub>2</sub>) (Atanga,<sup>3</sup> 2018) and oxidative dehydrogenation (ODH-O<sub>2</sub>) (Carrero,<sup>4</sup> 2014 and Shi,<sup>5</sup> 2018). Otroshchenko *et al.* recently reviewed the literature on metal oxide catalysts for each dehydrogenation reaction, including reaction-engineering and catalyst design, but omitted supported nanoparticle catalysts. To our knowledge there are no comprehensive literature reviews that compare and contrast non-oxidative and oxidative dehydrogenation reactions.

The scope of this article is to critically review the literature on DDH, ODH-CO<sub>2</sub> and ODH-O<sub>2</sub> to identify over-arching themes and common rules for catalyst design. We do not try

to capture aspects of reaction design and engineering, which itself is a vibrant field of research. We attempt to compare the performance of catalysts in the different sub-reactions by calculating a space time yield (STY), (measured in mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>), which is based on the initial activity of the catalysts. This enables a meaningful comparison between different research groups and reaction conditions. Additionally, we emphasise the environmental and industrial perspectives of each reaction and the prospects for industrial application.

## 1.2. Propene production processes – an environmental perspective

Traditionally, the industrial production of light alkenes, such as propene, has been carried out *via* either SC, or FCC of naphtha and diesel feedstocks. These methods typically provide a range of products including ethene, propene and gasoline, amongst others.<sup>6</sup> As of 2016, these routes accounted for 81% of propene production in industry, with 50% coming from SC and 31% from FCC. The remaining 19% was from newer technologies, such as direct dehydrogenation.<sup>6</sup>

SC, which involves the heating of fossil-fuels in the absence of oxygen to produce alkenes, requires temperatures up to 750–875 °C.<sup>7</sup> As an established process, naphtha SC has a high carbon efficiency, producing almost no CO<sub>2</sub> from the cracking process itself.<sup>7</sup> Although naphtha SC has an effective carbon efficiency, the process still relies on high temperatures for alkene production, which itself produces a significant amount of CO<sub>2</sub> from energy consumption.<sup>7,8</sup> These factors taken together result in steam cracking being responsible for the global emission of more than 300 million tonnes of CO<sub>2</sub> per year, as well as naphtha SC producing ozone-depleting CFCs.<sup>7</sup> FCC provides a way of producing light alkenes at lower temperatures compared to SC, by employing a catalyst into the process. However, despite its modestly lower operating temp-



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**Table 1** Summary of various propene production processes from a green chemistry perspective

Feedstock	Processes	Atom economy	Toxic reactants	Renewability of feedstock	GWP (kg CO <sub>2</sub> per kg C <sub>3</sub> H <sub>6</sub> ) <sup>a</sup>	Resource scarcity (USD per kg C <sub>3</sub> H <sub>6</sub> ) <sup>a</sup>	Human health (DALY per kg C <sub>3</sub> H <sub>6</sub> ) <sup>a</sup>	Ecosystem (species year per kg C <sub>3</sub> H <sub>6</sub> ) <sup>a</sup>
Naphtha	SC	Low	Crude oil/ naptha streams	Non-renewable	1.8	0.61	0.25	0.05
Coal	Syn gas, methanol synthesis, MTO	Low	Methanol	Non-renewable	16.5	0.60	4.0	1.1
Natural gas	Syn gas, methanol synthesis, MTO	Low	Methanol	Mostly non-renewable	4.5	1.10	0.8	0.2
Propane	DH	High	None	Mostly non-renewable	2.5	0.55	0.4	0.1

SC = steam cracking, GWP = global warming potential, DALY = disability-adjusted life years, MTO = methanol to olefins. <sup>a</sup> Values from ref. 11.

eratures, the FCC process produces many by-products. Many reduced S and N species are formed, as well as significant CO and HCN, which start forming at as low as 450 °C. Partial burn FCC reactors, (*i.e.*, reactors which form CO, rather than CO<sub>2</sub>) will incorporate a CO burner downstream.<sup>9</sup> Feedstocks involved in FCC processes typically include high molecular weight hydrocarbons, breaking them down into more valuable light alkenes; however, it often struggles to process lighter feedstocks such as naphtha.<sup>9</sup> Both processes are designed to produce a wide array of products, as well as often generating by-products that require additional energy to process. In addition, while propene demand is increasing, processing plants are tending towards higher ethene production due to shale gas production, leading towards a global shortage of propene.<sup>6,10</sup> Overall, cracking of naphtha and other petrochemical feedstocks to produce propene is unsustainable and leads to significant CO<sub>2</sub> emissions. Alternative indirect routes to propene, from *syn* gas and *via* methanol, has also gained interest in recent years.<sup>7</sup> The feedstock for this process can be biomass, shale gas or coal. Using coal as a feedstock has gained widespread use in China but poses a huge environmental burden.

The environmental and economic aspects of different existing propene production technologies are important consider-

ations when reviewing the feasibility of newer technologies based on dehydrogenation. Green chemistry principles, such as atom economy, the use of toxic chemicals and the renewability of the feedstock, are especially relevant. This is summarised in Table 1, which compares steam cracking, MTO (from coal and natural gas) and dehydrogenation. Atom economy is a measurement of the percentage of atomic mass in the starting reagents that ends up in the final product. It serves as a useful indicator of how chemically efficient a process *could* be. It is important to remember that in practice, the real atom economy is determined by the selectivity of the catalyst, and the prevalence of side-reactions. Although it is not possible to precisely calculate the atom economy of SC or MTO due to the complexity of the process and uncertainty in the composition of the feedstock, it is apparent that both of these technologies are inferior to dehydrogenation. In the case of SC a wide range of chemicals are made, and while these are ultimately utilised in the production of other chemicals, the % of propene formed from such a process is low. Equally, in the MTO process from coal or natural gas, the atom economy is limited by the generation of H<sub>2</sub>O as a by-product. In contrast, in the case of dehydrogenation only H<sub>2</sub> is generated as a by-product, meaning an atom economy of 95% is possible. With respect to the toxicity of the chemicals,

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SC forms various carcinogenic compounds, and the toxicity of methanol is well-established. In contrast, propane is non-hazardous. At present each of the feedstocks used in the main methods of propene production tend to be non-renewable. In the case of SC and coal-based MTO, this is unavoidable due to the nature of the feedstock. However, natural gas and propane can be produced from biomass. In these cases, the feedstock is renewable and so these processes are potentially much more sustainable than when using fossil fuels. Rodríguez-Vallejo *et al.* carried out life cycle analyses of naphtha cracking, propane dehydrogenation and MTO (using coal or natural gas as feedstocks).<sup>11</sup> In this analysis, the global warming potential (GWP), resource scarcity, impact on human health and the impact on the ecosystem was considered and quantified as a cost per kg of C<sub>3</sub>H<sub>6</sub> produced. These data are shown in Table 1. In terms of the global warming potential of each process, the MTO based reactions are clearly worse than the naphtha cracking or direct dehydrogenation reactions, but the CO<sub>2</sub> emissions of the coal-based feedstock is almost an order of magnitude higher than naphtha cracking. A similar trend was observed in the ecosystem category. This was measured in terms of local species lost integrated over time and underlines the gross negative impact of utilising coal as a feedstock in this chemistry. Resource scarcity was calculated based on the monetary burden of future mineral and fossil fuel extraction and shows that natural gas has around double the cost of that associated with propane, coal and naphtha. Finally, the cost to human health was estimated in terms of disability-adjusted life years, and naphtha cracking and propane dehydrogenation came out favourably compared to the MTO processes. Based on these metrics, it is clear that MTO from coal or natural gas has a larger environmental burden than SC or dehydrogenation. Opportunities for improving the sustainability of the

dehydrogenation process were recently highlighted by Agarwal *et al.* who investigated various intensification and integration strategies. It was shown that such strategies, which involved additional waste heat recovery and off-gas recycling, up to 70% reductions in CO<sub>2</sub> emissions were possible.<sup>12</sup>

The increased interest in direct propane dehydrogenation has been enhanced by the fall in propane price, which is the direct result of the discovery of vast shale gas reserves in North America. Although propane is a minor component in shale gas, it is facile to separate and therefore represents a valuable, but non-renewable source of propane. Increasing public pressure to move away from such non-renewable feedstocks continues to gain momentum and the propane production industry has responded accordingly. The production of renewable 'green' propane (also called bio-propane and bioLPG) is an emerging sector which is already being operated on a large scale. TotalEnergies operates a bio-refinery in La Mede, which has a design capacity for bio-propane of 25 000 tonnes per year.<sup>13</sup> Additionally, Neste recently opened a renewable propane production plant, which will produce 40 000 tonnes per year.<sup>14</sup> The propane generated is then sold on to be used in direct propane dehydrogenation.<sup>15</sup> While this is an important start, it represents less than 1% of annual propane capacity. Bio-propane can be produced from the processing of biomass, notably as a side-product in the production of biodiesel<sup>16</sup> as well as glycerol<sup>17</sup> and other substrates.<sup>18</sup> With increasing pressure to source chemical feedstocks sustainably, we can expect that new interest will focus on renewable and green routes to the key platform chemicals currently required by modern society, and that green propane will play an important role in this.

Overall, direct propane dehydrogenation satisfies many principles of green chemistry in comparison to SC and MTO benchmarks: it is highly atom-economic, does not use toxic



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reactants (or generate toxic by-products) and can in principle, utilise renewable feedstocks. However, in practice dehydrogenation will only be desirable as a means of producing propene if the reaction can operate efficiently, with minimal side-products and maximum yield. These factors are governed by the choice of catalyst, the main focus of the current review. The development of an active, selective and stable catalyst is essential for dehydrogenation to be considered as a viable process in the near- and long-term future.

## 2. Thermodynamics and environmental aspects of different dehydrogenation processes

Each dehydrogenation reaction has different thermodynamic, environmental and economic aspects, which are important to recognise when designing catalysts and sustainable processes. In section 1.2, the environmental implications of cracking and MTO were discussed and compared with DDH. The majority of analyses focus on well-established processes, where more information and data are available, but no such analyses were found for oxidative dehydrogenation. As a result, the environmental impact of these novel reactions can only be speculated upon. The following section focuses on the thermodynamic and environmental aspects of each sub-reaction, drawing on available literature whenever possible, and when not possible suggesting the most important aspects that could affect the sustainability of each process.

### 2.1 DDH

DDH is an endothermic reaction ( $\Delta H_{298}^{\circ} = 124 \text{ kJ mol}^{-1}$ ), which is equilibrium-limited at higher partial pressures of propane and lower reaction temperatures. As a result, typical

reaction temperatures for industrial DDH processes are 550–750 °C. Another key challenge in catalyst design for DDH is the fact that coke is also a favoured product under the conditions required for high propene yield and its formation is assumed to be initiated by deep dehydrogenation. Fig. 1 illustrates the typical reaction pathways observed in DDH. Catalytic and thermal (gas-phase radical) cracking reactions lead to the formation of methane and ethene. Ethene can then hydrogenate to ethane. The hydrogenolysis of propane is also possible, which forms methane and ethane.

As described above, the atom economy for DDH is high (95%) and the only by-product (in theory) is molecular hydrogen, which is a valuable resource with many uses and applications, not least as a carbon-free fuel. In practice however, frequent regeneration steps are required to remove coke, which involves combustion to form carbon dioxide. This means that the environmental impact of this process will depend to some extent on the prevalence of coke formation on the catalyst surface. As a feedstock,  $\text{C}_3\text{H}_8$  is non-toxic, unlike methanol in the MTO process. The high flammability of  $\text{C}_3\text{H}_8$  may present a safety risk in a chemical plant, but such a risk is present in all forms of  $\text{C}_3\text{H}_6$  production.

### 2.2 ODH- $\text{O}_2$

ODH- $\text{O}_2$  is exothermic ( $\Delta H_{298}^{\circ} = -117 \text{ kJ mol}^{-1}$ ) and conversion is not limited by thermodynamic equilibrium. Additionally, the formation of coke is suppressed substantially, with overoxidation constituting the main competing pathway. Fig. 2 shows the typical reaction pathways that occur over ODH- $\text{O}_2$  catalysts. Overoxidation is the main drawback, with CO and particularly  $\text{CO}_2$  reported as by-products. Cracking products are also reported, but generally as minor products. In common with ODH- $\text{CO}_2$ , water is formed *via* oxidative dehydrogenation.  $\text{CO}_2$  can also be formed *via* direct combustion of  $\text{C}_3\text{H}_8$ .<sup>19</sup>



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*2013, the ENI Award for Advanced Environmental Solutions in 2017, the RSC Faraday Lectureship and Prize in 2018, a CBE in the Queen's Birthday Honours List in 2018 and the Michel Boudart Award in 2021.*



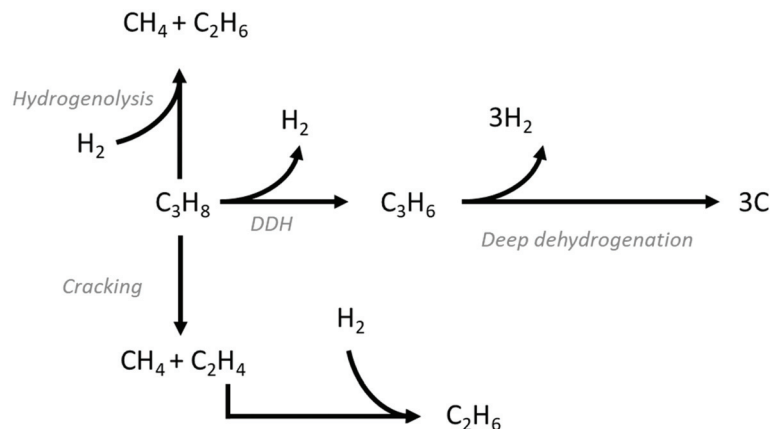


Fig. 1 Reaction pathways commonly observed during the DDH of propane. In addition to DDH, unfavourable deep dehydrogenation to coke, hydrogenolysis and cracking are also observed.

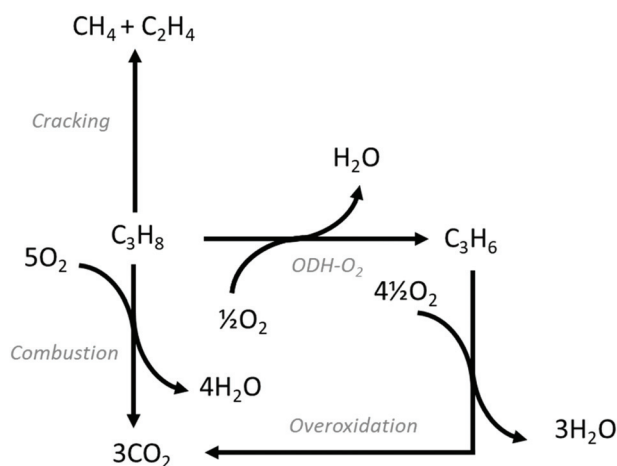


Fig. 2 Reaction pathways commonly observed in ODH-O<sub>2</sub> reactions. In addition to ODH-O<sub>2</sub>, overoxidation, combustion and cracking are often observed.

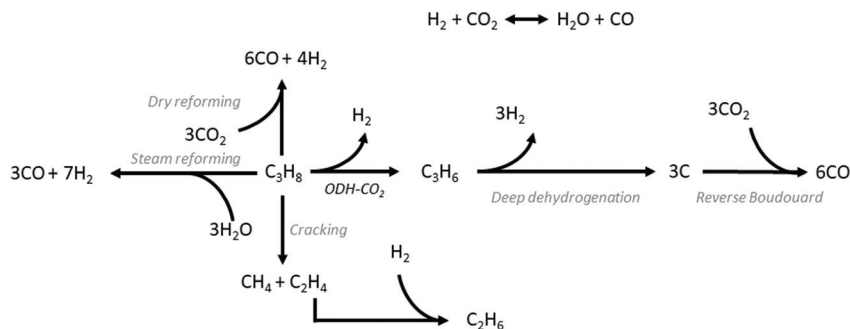
The addition of O<sub>2</sub> enables lower operating temperatures to be utilised (typically 450–550 °C) and is exothermic, meaning the energy costs of sustaining the reaction temperature are less than those in DDH and ODH-CO<sub>2</sub>. However, the atom economy of ODH-O<sub>2</sub> is 70% and H<sub>2</sub>O is generated as a by-product rather than H<sub>2</sub>. While CO<sub>2</sub> may be generated as a by-product, this depends on the catalyst, and the overall CO<sub>2</sub> generated may be comparable to a DDH process. There will be increased energy consumption associated with supplying the oxidant in sufficient purity and volume. If air is used, downstream separation of N<sub>2</sub> will be necessary, which would increase process energy consumption. The reactants and products are non-toxic, but the use of O<sub>2</sub> and C<sub>3</sub>H<sub>8</sub> introduce an elevated safety risk. Although an in-depth environmental analysis of an ODH-O<sub>2</sub> process for C<sub>3</sub>H<sub>8</sub> has not yet been carried out, it may be concluded that ODH-O<sub>2</sub> is comparable, if not more environmentally-friendly than DDH due to the lower expected costs associated with maintaining the reaction temp-

erature. However, the performance and composition of the catalyst will be a crucial factor in this comparison. The economic aspects of ODH-O<sub>2</sub> have not been analysed for C<sub>3</sub>H<sub>6</sub> production. However, the oxidative dehydrogenation of C<sub>2</sub>H<sub>6</sub> has been investigated extensively, and such an analysis is available. Gaffney and Mason compared ODH-O<sub>2</sub> of C<sub>2</sub>H<sub>6</sub> with thermal cracking and showed that ODH-O<sub>2</sub> has the potential to significantly reduce the plant capital costs and the overall cost of production.<sup>20</sup> Given the similarities in the cracking and dehydrogenation of ethane and propane, it is reasonable to conclude that the economic factors associated with the ODH-O<sub>2</sub> of C<sub>3</sub>H<sub>8</sub> are also favourable compared with steam cracking.

### 2.3 ODH-CO<sub>2</sub>

ODH-CO<sub>2</sub> is even more endothermic than DDH ( $\Delta H_{298}^{\circ} = 164 \text{ kJ mol}^{-1}$ ), due to the contribution of the mildly endothermic reverse water-gas shift (RWGS) reaction (Fig. 3). While it seems as though the addition of CO<sub>2</sub> would be detrimental on this basis, the removal of hydrogen *via* the RWGS reaction favourably shifts the thermodynamic equilibrium to enable higher propene yields. Hence, ODH-CO<sub>2</sub> can be carried out at lower reaction temperatures than DDH (450–600 °C). Although the reaction can proceed *via* a one-step oxidative dehydrogenation pathway or a two-step DDH + RWGS reaction, the net reaction is the same. A key competing reaction pathway in ODH-CO<sub>2</sub> is dry reforming of propane (DRP) (Fig. 3), which can occur under the same conditions as ODH-CO<sub>2</sub>.<sup>21</sup> In addition to DRP, CO<sub>2</sub> can react with coke to generate CO *via* the reverse Boudouard reaction, which is reported to proceed under typical reaction conditions for ODH-CO<sub>2</sub> (500–600 °C). Zangeneh *et al.*<sup>22</sup> carried out a full thermodynamic analysis of the ODH-CO<sub>2</sub> reaction, considering coke-forming and dry reforming side-reactions. The inclusion of these reactions in the thermodynamic model strongly impacted the equilibrium product of propene, increasing the equilibrium conversion of propane at the expense of propene selectivity. Dry reforming of propane was favoured at higher temperatures, while coke-formation was favoured at lower temperatures and at lower





**Fig. 3** Reaction pathways commonly observed in ODH- $\text{CO}_2$  reaction. In addition to ODH- $\text{CO}_2$ , deep dehydrogenation, cracking and in some catalysts dry reforming are observed. The reverse Boudouard reaction is also frequently reported to occur under typical reaction conditions.

$\text{CO}_2:\text{C}_3\text{H}_8$  ratios. It was also pointed out that the reported experimental data showed conversions well below equilibrium values, suggesting rapid catalyst deactivation. This analysis highlighted the need for kinetic control of dry reforming and coke forming reactions in order to maximise propene yield. Instead of hydrogen, water is formed either as the primary oxidative dehydrogenation product or as a result of DDH followed by the RWGS reaction.

From an environmental perspective, ODH- $\text{CO}_2$  has the greatest potential in the context of a circular economy. Although the formation of water is less desirable than hydrogen, ODH- $\text{CO}_2$  has the benefit of consuming  $\text{CO}_2$  in the process, and this is often cited as the motivation for investigating this route. Chemical  $\text{CO}_2$  utilisation is an attractive prospect in the context of combatting climate change: if  $\text{CO}_2$  can be consumed in large scale processes, the overall carbon footprint of certain products/technologies could be significantly reduced. However, it is important to consider how CO, which is formed from ODH- $\text{CO}_2$ , could be used in a sustainable way to justify the apparent greenness of ODH- $\text{CO}_2$ . If the CO is used in the water-gas shift (WGS) reaction for hydrogen production, then  $\text{CO}_2$  is immediately formed as a result, and the process becomes carbon neutral. Equally, if CO is combined with  $\text{H}_2$  to be used in various *syn*-gas processes, *e.g.* methanol or Fischer-Tropsch synthesis, then it is likely that the carbon will be burned as a fuel and ultimately returned to  $\text{CO}_2$ . While this may not be considered to be as desirable as sequestering  $\text{CO}_2$  from the atmosphere, the utilisation of  $\text{CO}_2$  in this technology would form part of a 'renewable carbon' cycle, and avoids additional  $\text{CO}_2$  emissions. This concept of carbon avoidance forms an important part of the short and medium term strategies to curb  $\text{CO}_2$  emissions, and carbon capture and storage technologies are a fundamental aspect of this.<sup>23</sup> The source of  $\text{CO}_2$  is also an important consideration.  $\text{CO}_2$  may be sequestered from the environment at additional process costs, or may be recovered from other  $\text{CO}_2$  forming processes. In comparison to other dehydrogenation reactions, ODH- $\text{CO}_2$  has the lowest atom economy (48%), but compared to cracking processes, where  $\text{C}_3\text{H}_6$  is a minor product, this is respectable. The overall efficiency of the reaction will also depend on the catalyst, and if the above undesirable pathways can be sufficiently minimised.

Overall, each dehydrogenation reaction has unique operating conditions and challenges, which are dictated by their thermodynamics. In the case of DDH, the formation of coke remains the biggest challenge, as it is thermodynamically favoured under conditions that enable high propane conversion. In ODH- $\text{CO}_2$ , dry reforming is also a competing pathway under typical reaction conditions and in the case of ODH- $\text{O}_2$ , overoxidation is prevalent due to  $\text{CO}_2$  being the thermodynamically favoured product. The thermodynamic tendency to form undesirable by-products means that such reactions must be carefully kinetically controlled. Careful catalyst design can inhibit and even switch-off some of these side-reactions, as will be discussed in the subsequent sections.

### 3. Commercial processes

The commercial dehydrogenation of propane is exclusively carried out in the absence of an oxidant. There are several technologies that currently operate, using various catalysts based on Pt or Cr, as shown in Table 2.

The Oleflex process from UOP employs alkali metal-promoted Pt-Sn/ $\text{Al}_2\text{O}_3$  catalysts in a reaction system composed of four moving bed reactors. In this process, the catalyst is continuously regenerated in a separate regeneration circuit. The reactors are connected in series with gas flow pre-heaters operating at pressures between 1 and 3 bar in the region of 650 °C. The typical catalyst in the Oleflex process consists of spherical pellets of  $\gamma\text{-Al}_2\text{O}_3$  (surface area *ca.* 100 m<sup>2</sup> g<sup>-1</sup>) containing Pt (<1 wt%) promoted with Sn and alkali metals.

The Dow FCDh technology utilises a fluidised reactor system coupled with a fluidised regeneration reactor, which enables continuous operation/regeneration.<sup>24</sup> The catalyst is comprised of a commercially available  $\text{Al}_2\text{O}_3$  support that is impregnated with Ga and Pt. The catalyst can be fully recoverable after the regeneration step, which involves high temperature oxidative treatment to remove retained carbon species *i.e.* coke. Compared with the Oleflex process, which requires a complicated regeneration protocol involving  $\text{Cl}_2$ ,  $\text{O}_2$  and then  $\text{H}_2$ , the Dow FCDh technology enables a much simpler regeneration cycle.





**Table 2** Commercial propane dehydrogenation technologies for a selection of catalysts.<sup>24,25</sup>

Technology Name	Oleflex	Dow FCDh	Uhde STAR Process	CATOFIN	K-PRO
Licensors/ developer	UOP LLC Honeywell	Dow	Krupp-Uhde	ABB Lummus	KBR, inc.
Reactor type	4 moving-bed reactors + 1 regeneration unit	Fluidised circulating reactor and regenerator	Adiabatic	Fixed bed parallel reactors	Orthoflow FCC continuous + continuous catalyst regeneration
Catalyst	Alkaline promoted Pt-Sn/Al <sub>2</sub> O <sub>3</sub>	Pt-Ga/Al <sub>2</sub> O <sub>3</sub>	Pt-Sn/ZnAl <sub>2</sub> O <sub>3</sub> /CaAl <sub>2</sub> O <sub>3</sub>	(Na/K) promoted CrO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	Proprietary – precious metal and Cr free
Catalyst Life	1–3 years	Unknown	Unknown	2–3 years	Unknown
Temperature/ °C	650	Unknown	550–590	560–650	Unknown
Pressure/bar	2–3	1.3–1.7	5–6	0.5	1.5
Cycle Time	5–10 days	<2 min	7 h (+1 h) regeneration	15 min	<1 min
Conversion/%	30–40	43–53	~40	48–53	45
Selectivity/%	84 (at 40% conversion)	92–96	~89	88	87–90

The Steam Active Reforming (STAR) process from Phillips Petroleum, developed by Uhde employs a Sn promoted Pt catalyst, (0.2 to 0.6 wt%), dispersed on a zinc–aluminate support, with a calcium/magnesium aluminate binder. The operating pressures and temperatures are between 6 and 9 bar and 550 to 590 °C, respectively.<sup>2</sup> Also, due to its non-acidic nature, the support does not promote undesired side reactions, such as cracking, isomerization or coke formation and contains Sn as a promoter to reduce coke formation and increase selectivity. Catalyst development for the STAR process continues: BASF and Thyssenkrupp announced a joint development agreement in 2020, which aims to reduce CO<sub>2</sub> emissions, reduce feed-stock consumption and the operating costs of the process. This underlines the opportunities in catalyst design in improving even already-commercialised processes.

Chromium oxide supported on aluminium oxide (CrO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>) is commonly employed industrially in the CATOFIN process and is composed of 18–20 wt% chromium oxide supported on 1–2 wt% alkaline metal (Na or K) promoted aluminium oxide.<sup>2,26</sup> The alkali promoter influences both the activity and selectivity of the catalyst by reducing the surface acidity of alumina, thus suppressing undesired side reactions. In the context of the commercialised CATOFIN process, improvements in the catalyst design and process conditions have been made, however challenges still exist relating to their activity, selectivity and stability. To boost the yield of propene and reduce emissions, the addition of a heat-generating material (HGM) has been employed, a notable example of which was developed by Clariant.<sup>27</sup> The exact composition of the HGM is likely to include copper oxide and additional promoters such as MnO<sub>2</sub>, supported on α-Al<sub>2</sub>O<sub>3</sub>.<sup>28</sup> This is loaded with the catalyst in the reactor, and is reduced during the reaction, which generates heat and therefore offsets the heat consumption that occurs during the DDH reaction. Since its rollout in 2015 in Ningbo Haiyue New Material Co., who are based in Ningbo City, China, the same HGM technology has been implemented in additional CATOFIN processes and Ineos recently awarded Clariant a long-term contract to supply the HGM.<sup>29</sup>

K-PRO was developed by KBR and is the latest process to be commercialised; the first contract was awarded in January 2020, around 1 year after the company introduced the technology and since then a licence has been agreed with JS Energy Ltd.<sup>30</sup> The significance of this process is that the catalyst does not contain precious metals or chromium, although the active component(s) remain proprietary information. The reactor is based on KBR's FCC orthoflow reactor, which is an up-flowing vertical reactor riser, conceptually similar to the Dow FCDh process in that the reactor is a fluidised bed, but the regeneration section is different.<sup>25</sup>

The commercial interest in further developing dehydrogenation technologies is evident from a simple examination of the patent literature. Fig. 4a shows the number of patents filed annually since 1980 that disclose inventions of novel catalysts for propane dehydrogenation. There is a marked increase over time, which has accelerated in the last decade. This growing interest and development are driven by the demand for propene itself, but also by the opportunity to further improve dehydrogenation catalysts. It is also evident from the sub-reaction breakdown that the majority (86%) of filed patents are for DDH catalysts, followed by ODH-O<sub>2</sub> (12%) and finally ODH-CO<sub>2</sub> (2.4%). Fig. 4b shows the breakdown of these patents by the 14 most prolific companies. China Petroleum & Chemical Corporation (SINOPEC) have published more patents than the next 13 companies combined, underlining the interest in direct propane dehydrogenation in the East Asia. It is also clear from this data that the interest in propane dehydrogenation is global, with companies from the USA, Europe and Asia all filing multiple patents.

## 4. Direct dehydrogenation

### 4.1. Pt-Based DDH catalysts

Platinum is the primary component in many dehydrogenation catalysts due to its ability to activate C–H bonds, coupled with its low activity for the breaking of C–C bonds. As shown above





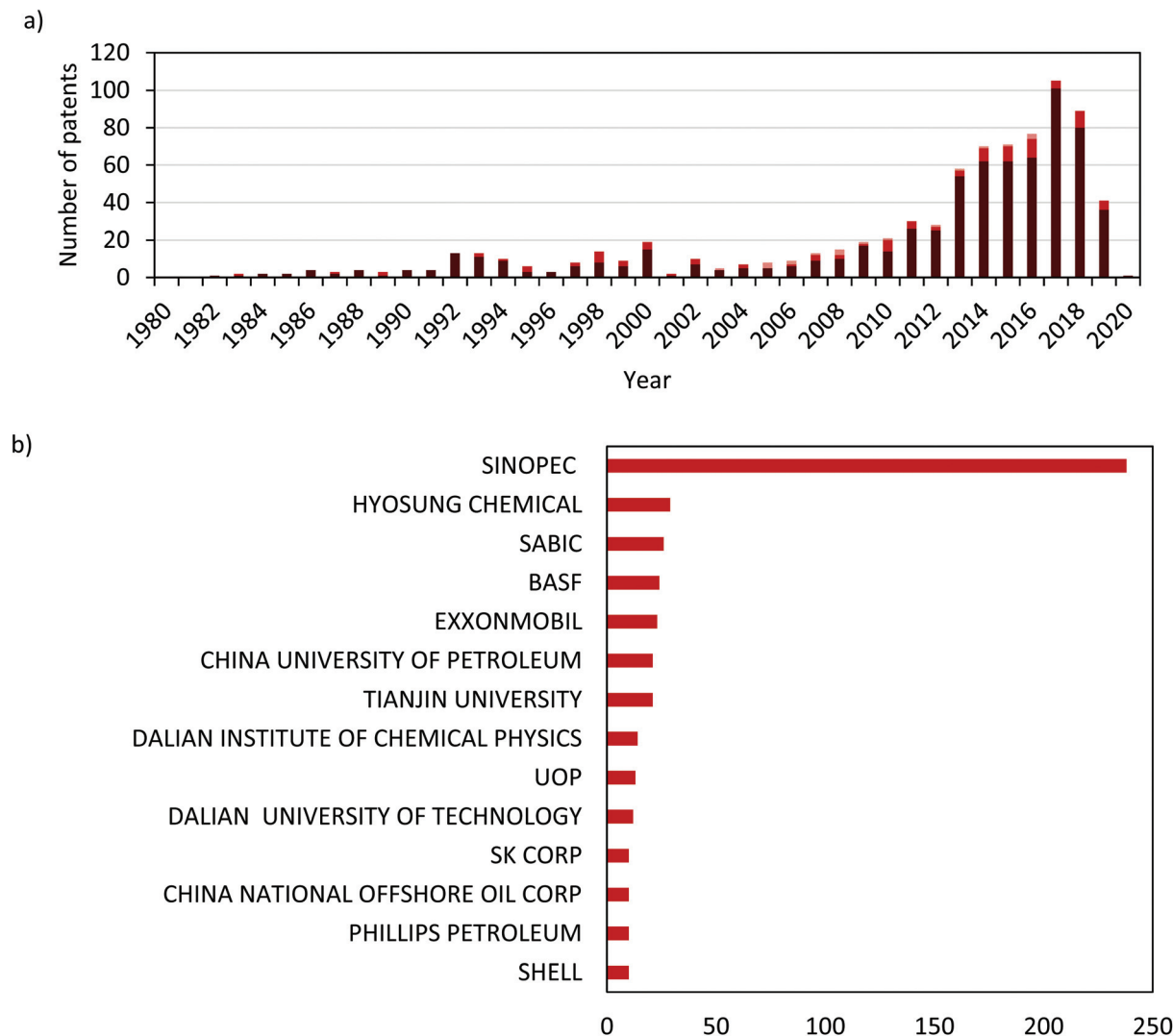


Fig. 4 (a) The number of patents published per year from 1980–2020 including the breakdown based on sub-reaction (DDH, dark red; ODH-O<sub>2</sub>, medium red and ODH-CO<sub>2</sub>, light red) and (b) the breakdown of patents filed per company for the top 14 companies active in this area.

in Table 1, Pt is present in three commercial processes. In this section, the most significant publications in the field of Pt-catalysed DDH are discussed.

The superiority of Pt as a DDH catalyst over other transition metals was recently illustrated by Araujo-Lopez *et al.* who used DFT calculations to measure the transition state energy for non-oxidative (and oxidative) C–H bond activation.<sup>31</sup> It was shown that Pt has the lowest value out of a range of transition metals, consistent with Pt typically outperforming other such metals experimentally. Interestingly, while Ag and Au did not facilitate non-oxidative C–H bond activation, in the presence of hydroxyl groups the energy barrier was much lower. These calculations help to explain the success of Pt catalysts for DDH and also highlight that other elements should be considered in ODH reactions.

The reaction mechanism for DDH has been the subject of much research. In describing catalytic dehydrogenation reac-

tions, the most commonly quoted mechanism is the Horiuti-Polanyi mechanism, proposed in 1934.<sup>32</sup> The mechanism proceeds as follows:

- Dissociative adsorption of the alkane (cleaving the first C–H bond).
- C–H cleavage of a second hydrogen from C<sub>3</sub>H<sub>7</sub>.
- Formation of a hydrogen molecule.
- Desorption of both hydrogen and the corresponding alkene.

The dissociative adsorption of propane and the C–H cleavage steps have been suggested as being rate-limiting,<sup>33</sup> although this depends on the catalyst. Due to the reaction conditions, side reactions frequently compete with the dehydrogenation reaction, reducing catalyst activity and selectivity. At high reaction temperatures, side reactions such as hydrogenolysis, cracking, aromatization and isomerization are thermodynamically and kinetically favoured.<sup>34–36</sup>

DDH is possible over almost all Pt sites, but the intrinsic selectivity and activity depends on Pt particle size: atomic steps and kink sites *i.e.* coordinatively-unsaturated species are responsible for C–H and C–C bond cleavage, which can take place here with near zero activation energy, leading to coke formation and thus catalyst deactivation.<sup>37–39</sup> While turnover frequency (TOF) increases as the Pt particle size decreases, selectivity is high in very small Pt species (<1 nm) and larger Pt nanoparticles (>3 nm).<sup>40</sup> A similar trend was also observed for stability, which is likely related to less selective Pt NPs forming coke more readily and blocking active sites.

One of the most fruitful areas of development in Pt-catalysed DDH is in the use of promoters. Specifically, Sn and Ga have been very successful, and this is reflected in their application in commercial processes, as discussed in section 3. The origin of the promotional effect of Sn has been discussed in detail in previous review articles.<sup>2,41</sup> Practically, the addition of Sn results in higher propene selectivity, lower support acidity, and increased diffusion of coke away from the active Pt site. Both geometric and electronic effects have been cited to explain these observations. Regarding geometric effects, Sn can modify the Pt particle size, which as previously discussed, strongly influences the reactivity of propane.<sup>42</sup> Specifically, Sn (oxide) can partially obscure the surface Pt species, which in turns creates smaller Pt ensembles. Regarding electronic effects, evidence for electron transfer from Sn to Pt has also been reported by DFT<sup>43</sup> and XPS analyses.<sup>44</sup> In an early report of Sn promoting Pt catalysts, Bari  s *et al.* demonstrated that the effect is support sensitive, in comparing Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/SiO<sub>2</sub>.<sup>45</sup> The addition of Sn to Pt/Al<sub>2</sub>O<sub>3</sub> was wholly beneficial, improving Pt dispersion and selectivity, while maintaining specific activity. Over Pt/SiO<sub>2</sub>, however, the Sn was more readily reduced and although an improvement in Pt dispersion and stability was noted, it came at the expense of specific activity. In fact, the oxidation state of Sn in the active catalyst is still debated and a range of different species may co-exist

from Sn<sup>4+</sup> through to Sn<sup>0</sup> before and during the DDH reaction.<sup>41</sup>

Pt promotion using Ga has also yielded highly active catalysts, and the role of Ga has been compared to that of Sn, *i.e.* due to both geometric and electronic effects. Wang *et al.* prepared a highly active Pt<sub>3</sub>-Ga/Al<sub>2</sub>O<sub>3</sub> catalyst and showed it could be improved by the addition of CeO<sub>2</sub>: Pt<sub>3</sub>-Ga/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> yielded an initial STY of 87 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>−1</sup> h<sup>−1</sup> (compared to 83 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>−1</sup> h<sup>−1</sup> without CeO<sub>2</sub>) (Table 3, entries 12 and 15).

Ge was recently shown to also boost the performance of Pt catalysts: Rimaz *et al.* prepared various Ge loadings, followed by reduction at different temperatures.<sup>46</sup> An initial propene yield of 53.8% was achieved on a Pt-Ge/Al<sub>2</sub>O<sub>3</sub> catalyst, comprising 0.5 wt% Pt and 1.5 wt% Ge reduced at 600 °C. The improvement of the bimetallic catalyst was ascribed to the electron withdrawing Ge promotor, which aided C–H activation. Isolated single Pt atoms in a Cu matrix (10 wt% Cu and 0.1 wt% Pt) supported on Al<sub>2</sub>O<sub>3</sub> simultaneously displayed enhanced catalyst activity, selectivity and stability over a 120 h period.<sup>47</sup> In producing supported single atom materials, undesired side-reactions were suppressed. Thus, isolated Pt atoms dispersed on Cu nanoparticles were identified as active centres with high propene selectivity; dramatically enhancing the desorption of surface bound propene, prohibiting its further dehydrogenation.

Numerous Pt-based catalysts supported on alumina (Al<sub>2</sub>O<sub>3</sub>) have been reported. The development of new catalysts with simultaneously enhanced activity, selectivity and stability is the ultimate goal. Gamma-alumina (γ-Al<sub>2</sub>O<sub>3</sub>) is characterized by a high number and density of medium-strong acid sites, which can lead to undesired side reactions. Br  nsted and Lewis acid sites on the support surface promote cracking and surface acid sites result in faster dehydrogenation for propene than propane, leading to deep dehydrogenation. Limited support acidity is needed to avoid undesirable side reactions, such as catalytic cracking and coke formation. However, Lewis

**Table 3** Comparison of the catalytic performance of selected Pt-based catalysts for DDH

Entry	Catalyst	T/�C	Feed composition	WHSV /h <sup>−1</sup>	X <sub>C<sub>3</sub>H<sub>8</sub></sub> /%	S <sub>C<sub>3</sub>H<sub>6</sub></sub> /%	STY /mol <sub>C<sub>3</sub>H<sub>6</sub></sub> kg <sub>cat</sub> <sup>−1</sup> h <sup>−1</sup>	Ref.
1	Pt/Mg(In)(Al)O <sub>x</sub>	550	C <sub>3</sub> H <sub>8</sub> = 100	1.6	24.2	98.2	7.8	54
2	Pt-Sn/B-ZrO <sub>2</sub>	550	C <sub>3</sub> H <sub>8</sub> /H <sub>2</sub> /N <sub>2</sub> = 1 : 1 : 8	1.8	36	97	13	69
3	Pt/Silicalite-1	550	C <sub>3</sub> H <sub>8</sub> /N <sub>2</sub> = 1 : 1	2.8	35	95	20	59
4	Pt <sub>3</sub> -Mn/SiO <sub>2</sub>	550	C <sub>3</sub> H <sub>8</sub> /N <sub>2</sub> = 1.25 : 98.75	29.5	6.8	95	41	65
5	Pt-Sn/Mg(3Zn)AlO	550	C <sub>3</sub> H <sub>8</sub> /N <sub>2</sub> = 1 : 4	3.8	55.2	99.4	47	56
6	Pt-Ga/Hd-Al <sub>2</sub> O <sub>3</sub>	580	C <sub>3</sub> H <sub>8</sub> /N <sub>2</sub> = 1 : 9	2.4	65.5	97	32	51
7	Pt/Al <sub>2</sub> O <sub>3</sub> -600	590	C <sub>3</sub> H <sub>8</sub> /H <sub>2</sub> /He = 1 : 1.25 : 4	5.2	48.5	96.9	51	50
8	Pt-Sn/Al <sub>2</sub> O <sub>3</sub> sheet	590	C <sub>3</sub> H <sub>8</sub> /H <sub>2</sub> /N <sub>2</sub> = 1 : 1.25 : 4	9.5	48.7	99.1	95	49
9	Pt-Cu/h-BN	600	C <sub>3</sub> H <sub>8</sub> /H <sub>2</sub> /N <sub>2</sub> = 1 : 1 : 3.9	4.0	24	97.3	20	70
10	Pt-In/LaAlO <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	600	C <sub>3</sub> H <sub>8</sub> /H <sub>2</sub> /N <sub>2</sub> = 8 : 7 : 35	2.6	47	96	26	53
11	Pt/TiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -10	600	C <sub>3</sub> H <sub>8</sub> /H <sub>2</sub> /N <sub>2</sub> = 1 : 1 : 1.85	10.2	47.3	78	80	52
12	Pt <sub>3</sub> -Ga/Al <sub>2</sub> O <sub>3</sub>	600	C <sub>3</sub> H <sub>8</sub> /H <sub>2</sub> /N <sub>2</sub> = 1 : 1 : 1.85	10.2	39.4	98	83	79
13	Pt-Zn@Silicalite-1	600	C <sub>3</sub> H <sub>8</sub> /N <sub>2</sub> = 1 : 1.73	6.5	45	99.8	66	63
14	Pt/TiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -20	600	C <sub>3</sub> H <sub>8</sub> /H <sub>2</sub> /N <sub>2</sub> = 1 : 1 : 1.85	10.2	45.5	88	86	52
15	Pt <sub>3</sub> -Ga/CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	600	C <sub>3</sub> H <sub>8</sub> /H <sub>2</sub> /N <sub>2</sub> = 1 : 1 : 1.85	10	41.1	98.5	87	79
16	Pt-In/Mg(Al)O <sub>x</sub>	620	C <sub>3</sub> H <sub>8</sub> /H <sub>2</sub> /Ar = 8 : 7 : 35	3.3	69	98	45	55

T = reaction temperature; feed composition = molar ratio of C<sub>3</sub>H<sub>8</sub>/H<sub>2</sub>/carrier in the reaction, X<sub>C<sub>3</sub>H<sub>8</sub></sub> = initial propane conversion, S<sub>C<sub>3</sub>H<sub>6</sub></sub> = initial propene selectivity, STY = space time yield. Hd = Hydrothermally synthesized.



acid sites and amphoteric –OH groups can function as nucleation sites for Pt, enhancing dispersion. This, coupled with the high specific surface areas frequently reported for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> explain its popularity as a catalyst support.<sup>48</sup> Recent advances in the use of numerous supports and catalysis synthesis methods for Pt-based catalysts and the underlying structure–activity correlations are considered below.

The importance of Al speciation in improving catalyst performance and stability was investigated by Shi *et al.* The effect of surface penta-coordinated (Al<sup>V</sup>), Al<sup>3+</sup> sites on a Pt–Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanosheet catalyst was investigated and after a 24 h reaction, a 4.1% drop in propane conversion with 45% propene yield was observed, corresponding to a STY of 95 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>–1</sup> h<sup>–1</sup> (Table 3, entry 8).<sup>49</sup> By comparison, the conventional Pt–Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst rapidly deactivated, retaining only 65% of its initial activity. The Pt–Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanosheet catalyst also exhibited enhanced activity due to the high proportion of Al<sup>V</sup> sites and their ability to uniformly disperse and stabilise Pt–Sn clusters.

Jang *et al.* explored calcination process parameters, namely temperatures of 600 °C and 750 °C, to modulate the surface properties of Pt–Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>50</sup> It was shown that calcination at 600 °C resulted in a 41.2% propene yield over a 20 h DDH reaction, equivalent to a STY of 51 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>–1</sup> h<sup>–1</sup> (Table 3, entry 7). The increased sintering resistance of the metal was ascribed to stabilization from the larger fraction of Al<sup>V</sup>, strong Lewis acid sites, which enhanced the metal–support interactions and suppressed coke deposition.

Yu *et al.* investigated the influence of sol–gel (Sg), hydrothermally synthesized (Hd) and commercially (C) obtained Al<sub>2</sub>O<sub>3</sub> in tuning the coordination structure of Al<sup>3+</sup> species in Pt–Ga/Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>51</sup> At 580 °C, initial propene yields of 63.5% and 57.5% were observed for Pt–Ga/Hd–Al<sub>2</sub>O<sub>3</sub> and Pt–Ga/Sg–Al<sub>2</sub>O<sub>3</sub>, respectively. Pt–Ga/Hd–Al<sub>2</sub>O<sub>3</sub> achieved a STY of 32 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>–1</sup> h<sup>–1</sup> (Table 2, entry 6). It was shown that Al<sup>V</sup> sites facilitate high dispersion of the active Pt and Ga ions, and result in strong metal–support interactions. Additionally, hydrogen spillover was more effective due to the increased dispersion, which aided the desorption of H<sub>2</sub> from the catalyst. This study demonstrated the importance of careful support preparation and the importance of the support surface in determining support metal nanoparticle dispersion and catalytic activity.

The modification of Al<sub>2</sub>O<sub>3</sub> with metal oxides, such as TiO<sub>2</sub><sup>52</sup> has been undertaken with some promising results. In the case of TiO<sub>2</sub>, it was shown that the addition of 10 and 20 wt% TiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> greatly enhanced the activity of the catalyst. The most active catalyst, a Pt/TiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst (with a TiO<sub>2</sub> loading of 20 wt%) exhibited an initial STY of 86 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>–1</sup> h<sup>–1</sup> (Table 3, entry 14). The enhanced performance was ascribed to electron transfer and acid site modulation effects resulting in changes to the adsorption properties of Pt. Similarly, Chen *et al.* reported a Pt–In/LaAlO<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with an initial STY of 26 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>–1</sup> h<sup>–1</sup> (Table 3, entry 10).<sup>53</sup>

Alternative supports, such as calcined hydrotalcite, Mg(Al)O<sub>x</sub>, have also been extensively investigated. Pt/Mg(Al)O<sub>x</sub> modi-

fied with In was prepared using the co-precipitation method by Tolek *et al.* At 550 °C, the catalyst achieved an initial propane conversion of 24.2% and 98.2% selectivity to propene.<sup>54</sup> This corresponded to a STY of 7.8 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>–1</sup> h<sup>–1</sup> (Table 3, entry 1). The Pt/Mg(In)(Al)O catalyst performance was attributed to a high fraction of metallic state In (In<sup>0</sup>) coupled with a high Pt dispersion with an average Pt particle size of 0.91 nm. Shen *et al.* prepared Pt/Mg(In)(Al)O catalysts, where promising results were obtained by altering the calcination temperature and Mg/Al ratio.<sup>55</sup> An optimised Mg/Al ratio of 4 led to an initial STY of 45 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>–1</sup> h<sup>–1</sup> at 620 °C (Table 3, entry 16). These optimised Pt/Mg(Al)O catalyst materials were characterised by having the lowest fraction of strong acid sites and highest specific surface areas. Wu *et al.* studied zinc-modified Pt–Sn/Mg(Al)O<sub>x</sub>, which exhibited an initial STY of 47 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>–1</sup> h<sup>–1</sup> (Table 3, entry 5).<sup>56</sup> Doping the support with an optimal amount of Zn resulted in smaller, and more uniformly dispersed metal particles distributed on the Mg(Al)O<sub>x</sub> support. Overall, there have been several attempts to enhance catalyst activity through introducing a second metal to Al<sub>2</sub>O<sub>3</sub> to form a mixed metal oxide support, or by preparing Al containing layered double hydroxides. Generally these have been shown to modestly boost catalyst performance, and the role of the second metal in most cases is to either enhance the dispersion of Pt, or adjust the acid–base properties of the support to inhibit side reactions.

Zeolites have been studied as potential supports for Pt-based catalysts due to their high surface areas, well-defined pore architectures and tuneable acid properties.<sup>57,58</sup> Wannapakdee *et al.* explored silicate-1 and Al<sub>2</sub>O<sub>3</sub> based mono-metallic Pt catalysts.<sup>59</sup> The performance over 10 h on-stream differed between the Pt/silicalite-1 and Pt/Al<sub>2</sub>O<sub>3</sub> materials, shown by >99% and 60% propene selectivity, respectively. The modified hierarchical pore structure, high specific surface area and presence of weak acid sites on Pt/silicalite-1 was concluded to be beneficial. Other zeolites which have been listed in patent literature for DDH of propane include Ta incorporated MCM-68, and H-ZSM-5.<sup>60,61</sup> In addition, non-zeolite porous silicates have been successfully applied to Pt nanoparticles.<sup>62</sup>

Pt–Zn nanoclusters encapsulated in silicalite-1 was investigated by Wang *et al.*, An initial STY of 66 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>–1</sup> h<sup>–1</sup> was measured, along with excellent cyclic stability during four DDH cycles at 600 °C (Table 3, entry 13).<sup>63</sup> Xu *et al.* evaluated a series of Pt–Sn/Si-beta catalysts with different Pt/Sn ratios at 570 °C and reported high initial propane conversions, *ca.* 50%, irrespective of Pt/Sn ratio.<sup>64</sup> The Pt–Sn<sub>2</sub>/Si-beta demonstrated an initial propene yield of 47.5%, which decreased by 3.4% over a 48 h reaction period, in contrast to the unmodified Pt/Si-beta catalyst which displayed a 47% reduction in the propene yield under identical reaction conditions. Through extensive characterisation the enhanced performance and stability was attributed to ultra-small, uniformly dispersed particles, ranging in size from 1.0 to 1.4 nm, consistent with previous studies that observed structure-sensitivity. It was found that embedding Sn in the zeolite framework was an effective



geometric diluter for Pt ensembles resulting in smaller, isolated Pt clusters which increase propene selectivity.

Wu *et al.* investigated the importance of sub-surface layers in supported nanoparticles. They reported that a Pt<sub>3</sub>-Mn/SiO<sub>2</sub> catalyst was enhanced by the presence of a Pt<sub>3</sub>-In subsurface layer (compared with a Pt subsurface layer). The optimised catalyst exhibited an initial STY of 41 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> (Table 3, entry 4).<sup>65</sup> Computational and experimental results suggested the role of the subsurface was to facilitate the activation of propane on the surface. Continuous testing for a week revealed long-term stability, and particle size distributions in the spent catalysts that were similar to those of the fresh catalysts. While the results in this work reveal a crucial role in the sub-surface composition of the catalyst, this aspect of catalyst design is often overlooked. Another sometimes neglected area of catalyst design is the role of heat treatments in modifying the nanostructure of the supported phase. Deng *et al.* reported highly selective Pt/SiO<sub>2</sub> and Pt-Sn/SiO<sub>2</sub> catalysts prepared under oxidative, reductive and inert atmospheres.<sup>66</sup> The Pt-Sn/SiO<sub>2</sub> materials prepared in inert and reductive atmospheres displayed initial propene yields of 17.8% and 25.7%, respectively. This was attributed to the reductive treatment and the presence of Sn which induced electronic and surface modifications of Pt nanoparticles following direct reduction in an H<sub>2</sub> atmosphere at temperatures in excess of 500 °C.<sup>67,68</sup>

Pt-Based catalysts supported on a boron-modified ZrO<sub>2</sub> have been reported by Miao *et al.*<sup>69</sup> The most active and stable catalyst, Pt-Sn/B-ZrO<sub>2</sub>, achieved a STY of 13 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, that was attributed to the moderate surface acidity of B-ZrO<sub>2</sub> (Table 3, entry 2). Wang *et al.* explored the use of hexagonal boron nitride (h-BN) nanosheets as a support for Pt-Cu clusters (with 0.01 wt% Pt and 1.0 wt% Cu loadings).<sup>70</sup> This afforded a STY of 20 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> at 600 °C, respectively (Table 3, entry 10). The role of Cu in the catalyst was to dilute the Pt species and promote desorption of propene, thereby enhancing selectivity. When tested under identical reaction conditions, this catalyst showed enhanced STY and stability compared to analogous catalysts supported on MgAl<sub>2</sub>O<sub>4</sub>, H-ZSM-5, SBA-15, SiC and Al<sub>2</sub>O<sub>3</sub>. The h-BN nanosheets provided abundant stacking fault edges terminated with B-O defects that are associated with unpaired electrons, which strongly interact with active metal species, helping to strengthen the interaction between the metal and support.<sup>71,72</sup>

Finally, other support materials which have been included in patent literature over the years have tried to improve upon the catalytic activity of those currently used in industrial processes. Support materials such as carbon nanotubes and nanodiamonds tend to impart good dispersion and high stability of Pt nanoparticles,<sup>73-75</sup> whereas a support made entirely of TiO<sub>2</sub> was shown to exhibit high activity while reducing carbon deposition.<sup>76</sup> Au and Sn supported Pt has also been investigated, as well as various metallic sulfide materials, all designed to increase the activity of the catalyst.<sup>77,78</sup>

In summary, supported Pt catalysts constitute a major category of DDH catalysts, and have been studied extensively.

Improvements in performance have been realised by tuning the particle size, promotion with other elements and selecting appropriate supports. Structure-activity relationships have been observed with regards to particle size, composition (presence of promotor/metal), as well as metal-support interactions. Control of these variables has been shown to influence the catalytic properties, and the reaction mechanism. Table 3 compares the activity of Pt catalysts over a wide range of conditions and with different supports and promoters. Pt-Sn and Pt-Ga supported on Al<sub>2</sub>O<sub>3</sub> (often but not always  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) are the most active in this class of DDH catalyst, which is unsurprising given their application in commercial catalysts. Additionally, the incorporation of Ti into an Al<sub>2</sub>O<sub>3</sub> support appears to boost activity significantly. Finally, Pt-Zn/silicalite-1 also exhibited a high STY, but Zn has not received the same attention as other promoters. Further studies may reveal that this bimetallic catalyst can compete with the current commercial catalysts.

#### 4.2. Cr-Oxide based DDH catalysts

Chromium oxide-based catalysts have been extensively studied for DDH since the pioneering work by Frey and Huppke in 1933.<sup>80</sup> This proved the importance of Cr<sub>2</sub>O<sub>3</sub> as a key catalyst component for the dehydrogenation of light alkanes to their corresponding alkenes at relatively high temperature and low pressure. Since the discovery of Cr-based dehydrogenation catalysts, several industrial companies have developed commercial dehydrogenation processes and catalysts.

Understanding the nature of the active chromium sites is fundamental to optimizing catalyst properties and limiting catalyst deactivation. Considerable research efforts have been undertaken to understand the nature of active sites and factors influencing catalytic performance in CrO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>81,82</sup> Spectroscopic analysis reveals a number of surface species with different oxidation states (Cr<sup>6+</sup>, Cr<sup>5+</sup>, Cr<sup>3+</sup>, Cr<sup>2+</sup>) and speciation (chromates, polychromates, crystalline and amorphous phases).<sup>83-86</sup> Weckhuysen *et al.* demonstrated that two types of surface chromium oxide species exist with differences in their reducibility: monomeric and polymeric species.<sup>87</sup> The relative concentration of different Cr surface species is strongly influenced by chromium loading and specific surface area of the selected support. Various studies have shown that low Cr loadings contribute to the dispersion of monomeric Cr<sup>6+</sup> species, with some Cr<sup>3+</sup> species and coordinative vacancies also being observed.<sup>88-91</sup> Meanwhile, at high Cr loadings, polymeric Cr<sup>3+</sup> species exist as clusters and/or crystalline Cr<sub>2</sub>O<sub>3</sub>. This limits the accessibility of the reactants to the Cr sites, thus limiting catalytic activity.

Therefore, different surface Cr species are known to coexist in the Cr-oxide based supported catalysts, causing differences in the catalytic performance for DDH. In particular, it has been reported that the redox cycle between active Cr<sup>6+</sup> and Cr<sup>3+</sup> species are responsible for the activity in the dehydrogenation reaction, but the reduction of Cr<sup>6+</sup> to Cr<sup>3+</sup> is rapid under reaction conditions.<sup>91-93</sup> Thus, dehydrogenation activity has been mostly attributed to monomeric Cr<sup>3+</sup> and less so to polymeric





$\text{Cr}^{3+}$  and  $\text{Cr}^{2+}$  sites produced in the initial steps of the DDH reaction. This is in agreement with De Rossi *et al.* who reported a correlation between DDH activity and the concentration of the coordinatively unsaturated  $\text{Cr}^{3+}$  species over  $\text{CrO}_x/\text{Al}_2\text{O}_3$  and  $\text{CrO}_x/\text{SiO}_2$  catalysts.<sup>94</sup> Additionally, through IR spectroscopy studies of CO and NO adsorption, the authors concluded that the most active  $\text{Cr}^{3+}$  species had two coordinative vacancies.

As described above, the Horiuti–Polanyi mechanism is widely accepted as the mechanism for the DDH reaction. However, an alternative dehydrogenation mechanism for Cr-based catalysts has been suggested,<sup>95,96</sup> which proceeds as follows:

- The formation of  $\text{Cr}^{3+}$ – $\text{C}_3\text{H}_8$  species.
- Heterolytic activation of the C–H bond of  $\text{Cr}^{3+}$ – $\text{C}_3\text{H}_8$  results in a  $\text{Cr}^{3+}$ – $\text{C}_3\text{H}_7$  intermediate.
- The  $\text{Cr}^{3+}$ – $\text{C}_3\text{H}_7$  intermediate undergoes  $\beta$ -H elimination to form  $\text{Cr}^{3+}$ – $\text{C}_3\text{H}_6 + \text{H}^-$  species.
- Propene desorption and formation of Cr–H species.
- Desorption of  $\text{H}_2$  due to proton transfer, completing the reaction cycle.

During the DDH process, the rate determining steps are the activation of the propane molecule to form the adsorbed  $\text{Cr}^{3+}$ – $\text{C}_3\text{H}_7$  intermediate, and the  $\beta$ -H transfer to form the  $\text{Cr}^{3+}$ – $\text{C}_3\text{H}_6$  hydride surface species which can significantly affect the DDH performance. In this instance, it is proposed that  $\text{Cr}^{3+}$ –O surface species can activate propane *via* sigma-bond metathesis by generating a Cr–alkyl intermediate that subsequently undergoes  $\beta$ -hydride elimination to form propene.<sup>92,95</sup>

As a catalyst support component,  $\text{Al}_2\text{O}_3$  has been widely used in alkane dehydrogenation processes due to its appropriate chemical properties, high structural stability and low cost. However, an inherent and major problem of the  $\text{CrO}_x/\text{Al}_2\text{O}_3$  catalyst system is rapid deactivation, which occurs as a consequence of coke formation. Cr nanoparticles dispersed on a series of rod-shaped porous alumina supports, followed by calcination at various temperatures ( $T$ ), denoted Cr–Al– $T$ , were prepared by Gao *et al.*<sup>97</sup> Catalytic tests, at 600 °C, revealed that Cr–Al–800 afforded an initial propene yield of 30%, from which it was inferred that the reducibility and lower surface acidity of

the Cr–Al–800 catalyst were advantageous, leading to a higher proportion of DDH active  $\text{Cr}^{3+}$  species and better anti-coking ability. Over the course of five dehydrogenation–regeneration cycles, the Cr–Al–800 catalyst demonstrated superior regenerative ability, and the initial STY was 60  $\text{mol}_{\text{C}_3\text{H}_6} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$  (Table 4, entry 9), which is comparable to many of the Pt catalysts reported in the literature.

Lang *et al.* compared the Cr loading in a number of  $\text{CrO}_x/\text{Al}_2\text{O}_3$  catalysts.<sup>98</sup> The 7.5 wt%  $\text{Cr}/\text{Al}_2\text{O}_3$  catalyst exhibited superior catalytic performance, exhibiting an initial propene selectivity and yield of 88.5% and 55.3%, respectively. This corresponded to a STY of 27  $\text{mol}_{\text{C}_3\text{H}_6} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$  (Table 4, entry 11). The surface  $\text{Cr}^{6+}/\text{Cr}^{3+}$  ratios produce differences in the reducibility of the catalysts and a direct correlation between increasing Cr metal loading and  $\text{Cr}^{6+}/\text{Cr}^{3+}$  ratios exists, leading to increased activity, decreased propene selectivity and excellent regenerative ability.

Węgrzyniak *et al.* investigated the influence of both mesoporous alumina and chromium metal loading in the range of 1–30 wt%.<sup>99</sup> The yield of propene achieved at 550 °C increased from 10.4 to 31.7% with 1 to 20 wt% Cr loading, however, further increase in Cr loading caused a decrease in the propene yield. The highest STY was achieved over the 20wt%  $\text{CrO}_x/\text{Al}_2\text{O}_3$  catalyst, which achieved 9.3  $\text{mol}_{\text{C}_3\text{H}_6} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$  (Table 4, entry 8), with a Cr concentration of 6.6 Cr atoms  $\text{nm}^{-2}$  which corresponded to 18% of Cr redox species. In agreement with catalytic activity, beyond this concentration of Cr the formation rate declines rapidly with the subsequent drop-in activity correlating well with the appearance of  $\alpha$ - $\text{Cr}_2\text{O}_3$  crystallites located outside of the mesopore system. The catalytic performance after four dehydrogenation–regeneration cycles of the 20 wt%  $\text{CrO}_x/\text{Al}_2\text{O}_3$  catalyst did not show any significant differences, demonstrating good long-term stability. The irreversible initial deactivation in the consecutive DDH cycles was attributed to either: (i) structural changes of active species (such as agglomeration), or (ii) collapse of pore structure.

Numerous efforts have been made to improve the performance of the  $\text{CrO}_x/\text{Al}_2\text{O}_3$  catalyst using different promoting elements. Notably, Zhang *et al.* reported the modification of a commercial  $\text{CrO}_x/\text{Al}_2\text{O}_3$  catalyst with Ce, which decreased the

**Table 4** Summary of catalytic performance over various reported Cr-based catalysts for DDH

Entry	Catalyst	$T/^\circ\text{C}$	Feed composition	WHSV / $\text{h}^{-1}$	$X_{\text{C}_3\text{H}_8}/\%$	$S_{\text{C}_3\text{H}_6}/\%$	STY/ $\text{mol}_{\text{C}_3\text{H}_6} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$	Ref.
1	$\text{Zn}_{0.3}\text{Cr}$	480	$\text{C}_3\text{H}_8/\text{Ar} = 1 : 19$	0.5	21	94	2.1	108
2	$\text{Cr}_{2.5}\text{Ni}_{5.0}/\text{Al}_2\text{O}_3$	550	$\text{C}_3\text{H}_8/\text{Ar} = 1 : 9$	1.2	47	95	11	101
3	$\text{Cr}_{10}\text{Zr}_{90}/\text{SiO}_2$	550	$\text{C}_3\text{H}_8/\text{N}_2 = 2 : 3$	4.3	15	95	13	103
4	$\text{Cr}_2\text{Zr}_{30}/\text{SiO}_2$ -600	550	$\text{C}_3\text{H}_8/\text{N}_2 = 2 : 3$	7.4	20	95	29	104
5	$\text{K-CrZr}_5\text{O}_x$	550	$\text{C}_3\text{H}_8/\text{He} = 1 : 14$	1.2	54	95	13	107
6	$\text{Cs-P/CrZrO}_x$	550	$\text{C}_3\text{H}_8/\text{N}_2 = 2 : 3$	5.9	30	97.5	38	106
7	$\text{CrO}_x/\text{H-ZSM-5}$ (260)	580	$\text{C}_3\text{H}_8/\text{N}_2 = 1 : 19$	0.6	60.8	78.2	5.9	102
8	$\text{CrO}_x/\text{Al}_2\text{O}_3$	600	$\text{C}_3\text{H}_8/\text{He} = 1 : 14$	1.2	41.8	89.8	9.3	99
9	$\text{CrO}_x/\text{Al}_2\text{O}_3$	600	$\text{C}_3\text{H}_8$	9.5	33.2	90.4	60	97
10	$\text{Cr}_{7.5}/\text{Al}_2\text{O}_3$	600	$\text{C}_3\text{H}_8/\text{Ar} = 1 : 4$	2.4	62.5	88.5	27	98
11	$\text{Ce-CrO}_x/\text{Al}_2\text{O}_3$	630	$\text{C}_3\text{H}_8/\text{N}_2 = 1 : 6.1$	1.2	86	78	17	100

$T$  = reaction temperature; feed composition = molar ratio of  $\text{C}_3\text{H}_8/\text{H}_2/\text{carrier}$  in the reaction,  $X_{\text{C}_3\text{H}_8}$  = initial propane conversion,  $S_{\text{C}_3\text{H}_6}$  = initial propene selectivity, STY = space time yield.



amount of inactive isolated  $\text{Cr}^{6+}$  sites.<sup>100</sup> This increased the amount of oxygen vacancies on the catalyst, thus promoting the interaction between Ce and Cr species. Consequently the  $\text{Ce-CrO}_x/\text{Al}_2\text{O}_3$  catalyst, when tested at 630 °C, displayed an STY of 17  $\text{mol}_{\text{C}_3\text{H}_6} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$  (Table 4, entry 12) and better regeneration ability over four cycles than that of the corresponding  $\text{CrO}_x/\text{Al}_2\text{O}_3$  catalyst over a single regeneration cycle.

Ni-Modified  $\text{CrO}_x/\gamma\text{-Al}_2\text{O}_3$  catalysts (5 wt% Ni and Cr loading) exhibited enhanced activity and selectivity to monometallic Ni/ $\gamma\text{-Al}_2\text{O}_3$  and  $\text{CrO}_x/\gamma\text{-Al}_2\text{O}_3$ , displaying an initial conversion of 47%, propene selectivity of 95% and yield of 44.7% at 550 °C. This equates to a STY of 11  $\text{mol}_{\text{C}_3\text{H}_6} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$  (Table 4, entry 2).<sup>101</sup> The presence of Ni promoted the formation of oligomeric Cr species and specifically  $\text{Cr}^{3+}$  active sites.

Other metal oxides have been utilised as supports for Cr-based catalysts in an attempt to improve the catalyst stability, including materials such as  $\text{ZrO}_2$ , mesoporous  $\text{SiO}_2$  and nanocarbons. He *et al.* investigated the effect of Cr loading on mesoporous MCM-41 with the  $\text{CrO}_x/\text{MCM-41}$  (10 wt% loading) catalyst displaying a propene yield of 47.5% at 630 °C.<sup>93</sup> FT-IR

analysis of this material suggested that high Cr loadings depleted surface hydroxyls, which were postulated to be essential for suppressing coke deposition.

The influence of surface acidity on activity has been investigated more in-depth by Hu *et al.* who prepared  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and H-ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 28, 43, 80$  and 260) supported Cr (5 wt%) catalysts.<sup>102</sup> Under identical reaction conditions, the  $\text{CrO}_x/\text{H-ZSM-5}$  (nominal  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio = 260) materials displayed better catalytic performance and stability than a commercial  $\text{CrO}_x/\text{Al}_2\text{O}_3$  catalyst, maintaining *ca.* 32.6% conversion and 94.2% propene selectivity after 50 h on stream. The authors attributed this enhanced performance to a high dispersion of Cr species, moderate acidity and strong metal-support interactions in the  $\text{CrO}_x/\text{H-ZSM-5(260)}$  catalyst. Fig. 5 illustrates the effect of surface acidity and Cr loading on the propene formation rate. Additionally, it was found that the  $\text{CrO}_x/\text{H-ZSM-5(260)}$  catalyst possessed strong anti-coking capability over long-term testing.

Moreover, Han *et al.* introduced Zr as a promoting element for Cr-catalysts on a number of supports ( $\text{Al}_2\text{O}_3$ ,  $\text{AlSiO}_x$ ,  $\text{SiTiO}_2$

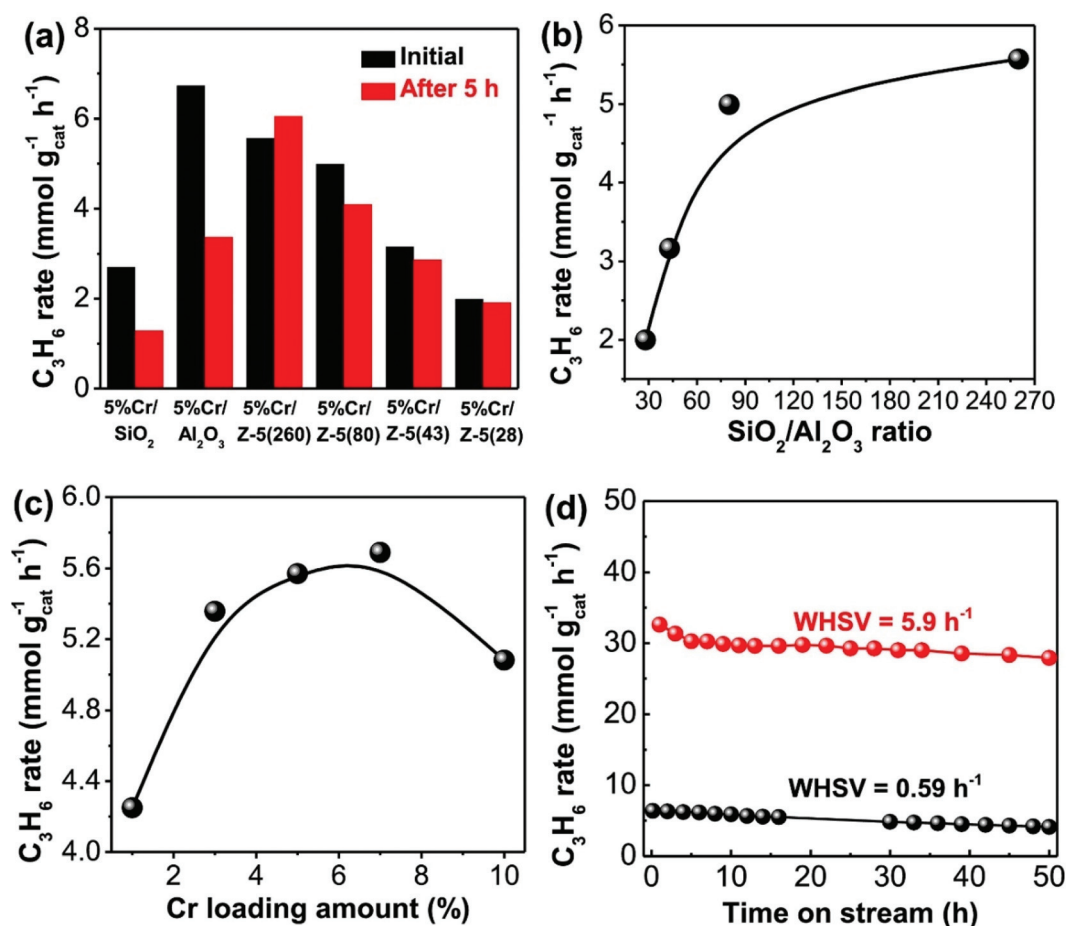


Fig. 5 Catalytic performance of the  $\text{CrO}_x$  catalysts on different supports. (a) Propene formation rates of the supported  $\text{CrO}_x$  catalysts before and after 5 h on-stream. (b) Initial propene formation rates of 5%  $\text{CrO}_x/\text{H-ZSM-5}$  catalysts as a function of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio. (c) Initial propene formation rates of  $\text{CrO}_x/\text{H-ZSM-5(260)}$  catalysts as a function of Cr loading amount. (d) Stability testing (propene formation rates) of 5%  $\text{CrO}_x/\text{H-ZSM-5(260)}$  catalyst at a WHSV of 0.59 and 5.9  $\text{h}^{-1}$  for 50 h time-on-stream. The tests in (a–c) were performed at a WHSV of 0.59  $\text{h}^{-1}$ . Reproduced from ref. 102 with permission from Elsevier.



and  $\text{SiO}_2$ ).<sup>103</sup> The Zr addition improved the turnover frequency for all Cr loadings when compared to analogous Cr-only catalysts and it was found that the greatest promotional effect was observed over the smallest  $\text{ZrO}_2$  crystallites. The order of reactivity was:  $\text{CrZr/SiO}_2 > \text{CrZr/AlSiO}_x > \text{CrZr/SiTiO}_x$ . Likewise, the degree of crystallinity in  $\text{CrZr/SiO}_2$  catalysts proved to be an important structural property affecting both the rates of propene and coke formation.<sup>104</sup> With increasing calcination temperature (450–600 °C) the catalysts displayed enhanced activity, selectivity and long-term stability (150 h) over consecutive dehydrogenation/regeneration cycles. However, the catalyst calcined at 600 °C exhibited a STY of 13  $\text{mol}_{\text{C}_3\text{H}_6} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$  (Table 4, entry 3).

Fujdala and Tilley reported  $\text{CrO}_x/\text{Si/Al/O}_x$  and  $\text{CrO}_x/\text{Si/Zr/O}_x$  catalysts exhibiting propene yields in excess of 33% at 450 °C.<sup>105</sup> Further improvements were observed when basic promoters (Cs and Ca) were added to  $\text{CrZr/Al}_2\text{O}_3$  catalysts which displayed a superior propene formation rate of 38  $\text{mol}_{\text{C}_3\text{H}_6} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$  after modification of the support with an acidic P-based modifier (Table 4, entry 6).<sup>106</sup> The positive effect was attributed to the promoters' ability to block the sites responsible for coke formation and negligible contribution to undesirable secondary reactions by the additional acid sites generated by the P-based modifier.

Mixed metal oxide catalysts have also been widely studied in the context of Cr-based catalysts. Węgrzyniak *et al.* demonstrated that ordered mesoporous Cr–Zr–O and Cr–Zr–K–O catalysts had improved catalytic performance compared to  $\text{CrO}_x/\text{Al}_2\text{O}_3$  materials and other promising catalysts in the DDH process.<sup>107</sup> It was found that all the catalysts modified with K displayed respectable regeneration ability as well as an improvement in the catalyst's STY, which was measured to be 13  $\text{mol}_{\text{C}_3\text{H}_6} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$  (Table 4, entry 5).

Another series of binary Zn–Cr mixed oxides with different Zn/Cr molar ratios (0–0.5) proved advantageous for the DDH reaction.<sup>108</sup> An optimal Zn/Cr ratio of 0.3 produced a highly active catalyst which displayed conversion, propene selectivity and propene yield values of 31.3%, 94% and 29.4%, respectively. The activity of the binary-component oxide catalyst was attributed to the defect-rich spinel structure, which generated a higher concentration of active  $\text{Cr}^{3+}$  species.

In summary, the dehydrogenation performance of  $\text{CrO}_x$ -based catalysts is largely influenced by the catalyst preparation method, identity of the support, as well as the promoting elements and active sites present in the resultant catalyst. The aforementioned factors influence activity, selectivity and stability and can be enhanced by optimizing elements of the catalyst design process. The most common deactivation pathway is coking, which can cause sintering in both the support and Cr. Efforts to improve catalyst design include using supports with ordered mesoporosity and moderate surface acidity, both of which aid mass transfer and avoid undesirable secondary reactions. Numerous Cr deposition methods have been explored, with novel surface organometallic chemistry methods emerging as viable preparation methods for ensuring isolated  $\text{CrO}_x$  species, although these may not be appropriate for large-scale

application. Promoting elements have been found to cause beneficial geometric and electronic effects on both the supports and  $\text{CrO}_x$  species. However, recent advances in unsupported, binary metal oxides have been successful in yielding catalysts with respectable activity, selectivity and resistance to coking. However, significant environmental and safety concerns still exist in the preparation, usage and disposal of  $\text{CrO}_x$ -based catalysts due to the associated toxicity. In comparison to Pt catalysts,  $\text{CrO}_x$  catalysts generally exhibit lower STYs, although the most active  $\text{CrO}_x$  catalysts (typically supported on  $\text{Al}_2\text{O}_3$ ) are as active as moderate supported Pt catalysts.

### 4.3. Ga-Based DDH catalysts

Historically, a bifunctional Ga/H-ZSM-5 material has been applied as a catalyst for the commercial process for propane aromatization, developed jointly by UOP and BP as the Cyclar Process.<sup>109,110</sup> More recently, the Dow FCDh process was developed which uses a Pt–Ga based catalyst. Gallium oxide ( $\text{GaO}_x$ )-based catalysts have been the subject of intensive research as candidate catalysts and/or supports for the DDH reaction. This is because Ga is another non-noble metallic element known to catalyse the dehydrogenation of propane, usually through oxidic, tetrahedrally coordinated  $\text{Ga}^{3+}$  species, which are considered to be active sites for C–H activation.<sup>111,112</sup> However, several surface gallium species (*e.g.*,  $\text{Ga}_2\text{O}_3$ ,  $\text{GaO}^+$  and  $\text{Ga}^{\text{n+}}$ ) can exist and are considered active constituents exhibiting different performance for the DDH reaction. Furthermore, the types of surface Ga species present are dependent on the identity of the support, Ga loading, as well as the preparation method.

Numerous studies have shown that  $\text{Ga}_2\text{O}_3$  dispersed on  $\text{TiO}_2$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ , H-ZSM-5, ZSM-8 and MWW zeolites display distinctly different catalytic properties for alkane dehydrogenation.<sup>113–116</sup> Sattler *et al.* reported a Pt-promoted  $\text{Ga}/\gamma\text{-Al}_2\text{O}_3$  species ( $\text{Pt}_3\text{Ga}/\gamma\text{-Al}_2\text{O}_3$ ) as a highly promising catalyst for propane dehydrogenation, which showed remarkably high activity, selectivity, and long-term stability.<sup>117</sup> For catalysts containing both Ga and a low amount of Pt (~0.1 wt%), the observed conversion was close to the equilibrium value, 55% at 620 °C with the addition of Pt as a promoter facilitating recombination of hydrogen atoms into  $\text{H}_2$ . By modulating the support acidity further with a K-dopant, the resultant  $\text{Pt}_3\text{GaK}/\gamma\text{-Al}_2\text{O}_3$  catalyst demonstrated enhanced stability, displaying a propane conversion of 31.1% and a selectivity for propene of 92.6% after approximately 150 cycles or 14 days of operation. The authors postulated the main active site for C–H activation was  $\text{Ga}^{3+}$  embedded within the  $\gamma\text{-Al}_2\text{O}_3$  framework.

Further investigations by Searles *et al.* showed that a  $\text{Ga}^{\delta+}\text{Pt}^0/\text{SiO}_2$  catalyst, featuring a highly dispersed  $\text{Ga}_x\text{Pt}$  alloy structure, had a long-term stability evident in unchanged propene selectivity (>99%) over the course of a 20 h DDH reaction.<sup>118</sup> Both the moderate surface acidity of the support and good dispersion of the generated gallium single-sites proved beneficial. Additionally, the monometallic  $\text{Ga}^{3+}/\text{SiO}_2$  catalyst also displayed minimal deactivation over a 20 h DDH reaction, retaining a high propene selectivity (94%) throughout.



A comparative approach to study the effect of the support acidity was taken by Szeto *et al.* through which marked differences were observed in the reactivity of silica and alumina supported Ga catalysts.<sup>119</sup> An initial conversion and selectivity of 24% and 79%, respectively, were reported for Ga/Al<sub>2</sub>O<sub>3</sub>. The STY was 5.9 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sup>-1</sup><sub>cat</sub> h<sup>-1</sup> (Table 5, entry 4). On the other hand, the Ga/SiO<sub>2</sub> catalyst was reported to have low activity (8% conversion initially) and moderately high selectivity to propene (90%) under identical testing conditions. This highlights the importance of selecting an appropriate support for different active centres.

Cybulskis *et al.* reported that the preparation strategy could greatly influence the structure of Ga/SiO<sub>2</sub> catalysts.<sup>120</sup> Utilizing a pH-controlled incipient-wetness impregnation method the resultant catalyst contained a high proportion of isolated Lewis acidic Ga<sup>3+</sup> sites dispersed on SiO<sub>2</sub>, with the ability to activate hydrocarbon C–H bonds with up to 99% selectivity through a non-redox pathway at 550 °C. A variety of spectroscopic characterisation methods further verified isolated four-coordinate Ga<sup>3+</sup>–O centres as catalytically relevant sites in these Ga/SiO<sub>2</sub> catalysts. Meanwhile the Ga<sup>δ+</sup>–H and Ga<sup>δ+</sup>–O species, which were identified as spectators, remained stable in inert and reductive atmospheres from room temperature to 550 °C, before reversibly decomposing in the presence of C<sub>3</sub>H<sub>6</sub> under reaction conditions to regenerate the Lewis acidic Ga<sup>3+</sup>–O centres.

Other supports (H-ZSM-5, SBA-15, γ-Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>) and the effect of Ga loading have also been investigated. Shao *et al.* established an optimal Ga loading of 5 wt%, reporting an initial propene yield on different supports that followed the trend: Ga/H-ZSM-5 (48%) > Ga/γ-Al<sub>2</sub>O<sub>3</sub> (43%) > Ga/SBA-15 (28%) > Ga/SiO<sub>2</sub> (9%) (Table 5, entries 7–9).<sup>121</sup> This was attributed to differences in surface acidity between supports, with strong acid sites largely determining the dispersion of Ga species, as well as inducing adverse side reactions. Zeolite supports can in principle hinder the formation of large hydrocarbon molecules due to their unique framework and channel structure, which are beneficial to the catalytic stability. Consequently, it was found that the Ga/H-ZSM-5 catalyst displayed the highest initial activity but lowest stability. Factors such as the highest specific surface area and lowest acidity were associated with the superior catalytic stability of the Ga/SBA-15 catalyst over the 30 h DDH reaction at 620 °C.

Further improvements reported by Kim *et al.* explored the catalytic function of Ga-based catalysts supported on bulk and hierarchical MFI-type zeolites, where Ga was used in place of Al.<sup>122</sup> Catalytic testing at 600 °C revealed substantial activity, selectivity and stability improvements in hierarchical Ga/MFI relative to the corresponding bulk Ga/MFI catalyst. The authors hypothesized that the enhanced activity and selectivity of the hierarchical catalysts arose from their quasi-2D structure and lower surface acidity. Generally, it is accepted that lowering the surface acidity can further enhance the catalytic performance of a DDH catalyst. The addition of 3-mercaptopropyl-trimethoxysilane (MPS) reduces Brønsted and increases Lewis acid sites in the preparation Ga/MFI catalysts, which resulted in improved performance.<sup>123</sup> When compared to a CrO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, the Ga/MFI catalyst, although less selective, was more stable and retained the moderate propene selectivity over the 12 h DDH reaction. Acidity characterization techniques confirmed a high concentration of strong Lewis acid sites and a reduction in the concentration of Brønsted acid sites in the Ga-MFI catalyst (Table 5, entries 5 and 6).

Schreiber *et al.* further verified the active sites for MFI supported Ga catalysts with moderate acidity, reporting an optimal Ga/Al ratio of 0.5, which enhanced the dehydrogenation rate.<sup>124</sup> The authors attributed high Ga/Al ratios (>0.5) with the formation of additional Ga<sub>x</sub>O<sub>y</sub> clusters which negatively affected the dehydrogenation rate and thus catalytic performance. Therefore, for Ga/MFI zeolites a synergy between Ga<sup>+</sup> species and a Brønsted acid site (BAS) (optimised to one Ga<sup>+</sup> per BAS) exists forming a Lewis–Brønsted acid pair during the dehydrogenation of propane. DFT calculations indicated that the generated Lewis–Brønsted acid pair is much more active than an isolated Ga<sup>+</sup>, due to the large increase in Lewis acidity upon protonation of Ga<sup>+</sup> by the BAS, which facilitates heterolytic C–H bond activation. The BAS also significantly reduces the activation barrier for H<sub>2</sub> elimination by recombination with a hydride. This was in agreement with findings by Phadke *et al.*<sup>125</sup>

Using a different approach, Raman *et al.* reported the synthesis of Ga–Rh supported catalytically active liquid metal solutions.<sup>126</sup> A correlation between alloy composition and specific activity was observed with Ga<sub>125</sub>–Rh exhibiting STYs of 5.0 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> (Table 5, entry 1). Bauer *et al.* reported

**Table 5** Performance of selected Ga-based catalysts for the DDH reaction

Entry	Catalyst	T/°C	Feed composition	WHSV /g <sub>C<sub>3</sub>H<sub>8</sub></sub> g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	X <sub>C<sub>3</sub>H<sub>8</sub></sub> /%	S <sub>C<sub>3</sub>H<sub>6</sub></sub> /%	STY/mol <sub>C<sub>3</sub>H<sub>6</sub></sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	Ref.
2	Ga <sub>125</sub> –Rh	450	C <sub>3</sub> H <sub>8</sub> /He = 1 : 9	0.88	29	95	5.0	126
3	Ga/SiO <sub>2</sub>	550	C <sub>3</sub> H <sub>8</sub> /Ar = 1 : 4	2.4	10	90	4.5	49
4	Ga/Al <sub>2</sub> O <sub>3</sub>	550	C <sub>3</sub> H <sub>8</sub> /Ar = 1 : 4	1.5	24	79	5.9	119
5	Ga-MFI	600	C <sub>3</sub> H <sub>8</sub> /Ar = 1 : 19	0.79	41	75	3.7	123
6	Ga-MFI	600	C <sub>3</sub> H <sub>8</sub> /Ar = 1 : 19	2.4	12.2	82	4.9	122
7	Ga/SBA-15	620	C <sub>3</sub> H <sub>8</sub> /Ar = 1 : 19	0.6	29.7	92	3.3	121
8	Ga/Al <sub>2</sub> O <sub>3</sub>	620	C <sub>3</sub> H <sub>8</sub> /Ar = 1 : 19	0.6	46	95.2	5.5	121
9	Ga/H-ZSM-5	620	C <sub>3</sub> H <sub>8</sub> /Ar = 1 : 19	0.6	78.1	60.2	5.9	121

T = reaction temperature; feed composition = molar ratio of C<sub>3</sub>H<sub>8</sub>/H<sub>2</sub>/carrier in the reaction, X<sub>C<sub>3</sub>H<sub>8</sub></sub> = initial propane conversion, S<sub>C<sub>3</sub>H<sub>6</sub></sub> = initial propene selectivity, STY = space time yield.





that an alternative liquid metal solution, Ga<sub>37</sub>-Pt/Al<sub>2</sub>O<sub>3</sub>, exhibited propane conversion as low as 350 °C.<sup>127</sup> The Ga-Pt alloy melts at temperatures between 270 °C and 330 °C.<sup>20</sup> At 400 °C and 450 °C, selectivity to propene was *ca.* 95% and 90%, respectively and activity was attributed to isolated Pt atoms in the supported liquid Ga-Pt alloy.

In summary, GaO<sub>x</sub> based catalysts are promising propane dehydrogenation candidates. However, these catalysts are limited by deactivation through coke formation and the sintering of GaO<sub>x</sub> species which are dependent on the support, Ga loading and preparation method. Studies have also shown the advantages of incorporating promoter elements and/or the formation of intermetallic alloys in enhancing the dehydrogenation performance. Ga catalysts generally exhibit STYs that are one order of magnitude lower than Pt catalysts, and the most active CrO<sub>x</sub> catalysts, but have the advantage of being benign and inexpensive.

#### 4.4. V-Based DDH catalysts

Vanadium-based catalysts have garnered increased interest as alternative materials to Pt- and Cr-based catalysts for the DDH reaction, to their comparative low cost and toxicity. Numerous studies have elucidated the effect of the preparation method, vanadium loading, promoter and support characteristics on the surface chemistry and catalyst performance of vanadium species.<sup>128–131</sup> Generally, the oxidation state of vanadium (*i.e.*, V<sup>3+</sup>, V<sup>4+</sup>, V<sup>5+</sup>) determines the catalytic activity.<sup>132</sup> In addition, the distribution of V oxidation states is controlled by the V loading, which in turn influences the degree of polymerization. It has been reported that V<sup>5+</sup> is the least active, whereas V<sup>4+</sup> and V<sup>3+</sup> species (generated from the reduction of V<sup>5+</sup>) are more active in the DDH reaction.<sup>133–137</sup> Additionally, these studies suggest that a number of VO<sub>x</sub> species exist including monovanadate (isolated V), polyvanadate (oligomeric V<sup>n+</sup>) and V<sub>2</sub>O<sub>5</sub> crystallites.

The nature of the support is an essential parameter to consider as several possible VO<sub>x</sub> can species exist. It is generally accepted that the metal-support (V–O–support) interactions affect the resultant catalyst performance.<sup>138</sup> It is proposed that V–O–support bonds are active sites, as lattice oxygen in V–O

bonds directly catalyses C–H activation forming H<sub>2</sub>. The activity is dependent on the bond strength of the V–O–support bond. Therefore, it is expected that catalyst performance is affected when different supports, such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> are utilised.

From a comparison of VO<sub>x</sub>/MCM-41, CrO<sub>x</sub>/MCM-41 and Pt–Sn/Al<sub>2</sub>O<sub>3</sub> catalysts, it was shown that VO<sub>x</sub>/MCM-41 exhibited superior propene selectivity (above 90%) and stability during several successive dehydrogenation–regeneration cycles.<sup>90</sup> Subsequent studies expounded on the importance of the support surface acidity on a range of aluminosilicates with varying SiO<sub>2</sub> contents.<sup>139</sup> Sokolov *et al.* investigated the effect of the support on the stability of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and AlSiO<sub>x</sub> supported VO<sub>x</sub> catalyst. It was reported that at 1 wt% V/AlSiO<sub>x</sub> (with 10 wt% SiO<sub>2</sub> in the support) was only around 25% less active than a Pt–Sn/Al<sub>2</sub>O<sub>3</sub> comparison sample. However, the STY of this most active catalyst at 550 °C was 5.1 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sup>−1</sup><sub>cat</sub> h<sup>−1</sup> (Table 6, entry 1), which is an order of magnitude below the values commonly reported for supported Pt catalysts tested at 600 °C, suggesting that more active Pt–Sn catalysts can be prepared than the one reported in this work. The catalyst deactivated quickly due to carbon deposition, but retained its initial activity over the course of ten successive dehydrogenation–regeneration cycles. The authors observed a positive correlation between the rate of coke formation and the acidity of the support, as well as reporting that coke can actually catalyse the DDH reaction. Additional studies attributed the dependence of coke formation on the degree of polymerization of VO<sub>x</sub> species over catalysts supported on a range of aluminosilicates, with differing SiO<sub>2</sub> contents varying from 1 to 100 wt%.<sup>140</sup> It was concluded that coke preferentially formed on larger V<sub>2</sub>O<sub>5</sub> crystallites rather than small or isolated VO<sub>x</sub> species.

The cation–anion double hydrolysis approach (CADH), used for the synthesis of mesoporous Al<sub>2</sub>O<sub>3</sub> with high surface area and a pure γ-Al<sub>2</sub>O<sub>3</sub> phase, was undertaken with the crystallisation temperature varied between 25–120 °C.<sup>141</sup> It was found that the crystallisation temperature of the support directly influenced the catalytic performance of the VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts, which was a consequence of the increase in Lewis acid

**Table 6** Catalytic performance of selected vanadia-based catalysts for the DDH reaction

Entry	Catalyst	T/°C	Feed composition	WHSV/g <sub>C<sub>3</sub>H<sub>8</sub></sub> g <sub>cat</sub> <sup>−1</sup> h <sup>−1</sup>	X <sub>C<sub>3</sub>H<sub>8</sub></sub> /%	S <sub>C<sub>3</sub>H<sub>6</sub></sub> /%	STY/mol <sub>C<sub>3</sub>H<sub>6</sub></sub> kg <sup>−1</sup> <sub>cat</sub> h <sup>−1</sup>	Ref.
1	V/SiO <sub>2</sub>	550	C <sub>3</sub> H <sub>8</sub> /N <sub>2</sub> = 2 : 3	0.95	30	85	5.1	139
2	VZrO <sub>2</sub>	550	C <sub>3</sub> H <sub>8</sub> /H <sub>2</sub> /N <sub>2</sub> = 1 : 1 : 5.1	2.06	25	85	9.2	149
3	VZrO <sub>2</sub>	550	C <sub>3</sub> H <sub>8</sub> /Ar = 1 : 6.5	4.7	25	98	24	150
4	V-SiO <sub>2</sub>	580	C <sub>3</sub> H <sub>8</sub> /Ar = 1 : 10	0.59	64	90	7.9	145
5	VO <sub>x</sub> /SiO <sub>2</sub>	580	C <sub>3</sub> H <sub>8</sub> /Ar = 1 : 10	0.6	55	91	6.2	147
6	7VO <sub>x</sub> /Si-Beta	600	C <sub>3</sub> H <sub>8</sub> /N <sub>2</sub> = 1 : 19	0.6	40	90	4.4	148
7	VO <sub>x</sub> -Mg/Al <sub>2</sub> O <sub>3</sub>	600	C <sub>3</sub> H <sub>8</sub> /H <sub>2</sub> /N <sub>2</sub> = 1 : 1 : 1.6	1.3	31	85	7.8	143
8	V-DMSN	600	C <sub>3</sub> H <sub>8</sub> /N <sub>2</sub> = 1 : 7.5	6.7	18.1	91	22	146
9	VO <sub>x</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	600	C <sub>3</sub> H <sub>8</sub> /H <sub>2</sub> /N <sub>2</sub> = 1 : 1 : 1.6	3.3	15	94	15	132
10	VO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	610	C <sub>3</sub> H <sub>8</sub> /N <sub>2</sub> = 4 : 1	2.8	30	85	15	141

T = reaction temperature; feed composition = molar ratio of C<sub>3</sub>H<sub>8</sub>/H<sub>2</sub>/carrier in the reaction, X<sub>C<sub>3</sub>H<sub>8</sub></sub> = initial propane conversion, S<sub>C<sub>3</sub>H<sub>6</sub></sub> = initial propene selectivity, STY = space time yield. DMSN = dendritic mesoporous silica nanoparticles.



sites with increasing crystallization temperatures up to 100 °C. This in turn affected the distribution of different surface V species. After an induction time of 1 h, the VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst (crystallized at 100 °C) achieved the best performance giving a propene yield of 60%, equivalent to a STY of 15 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sup>-1</sup><sub>cat</sub> h<sup>-1</sup> (Table 6, entry 10).

Similar studies investigating V loading (1–20 wt%) and its effect on the surface V species present in VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts reported a volcano plot-type trend between V loading and catalytic performance, with maximum activity being observed at 12 wt% V loading.<sup>132</sup> The authors concluded that the relative proportions of V<sup>3+</sup>, V<sup>4+</sup> and V<sup>5+</sup> species present on the catalyst surface were affected by V loading and at the optimal loading of 12 wt%, a high concentration of isolated V<sup>3+</sup> species was detected. *In situ* DRIFTS analysis elucidated the mechanistic pathway, whereby a vanadium propyl intermediate is formed after propane activation and rapidly transforms to propenyl-vanadium. Propene is formed from propenyl-vanadium or propyl-vanadium and desorbs from the catalyst surface.

Gu *et al.* reported that P modification could greatly influence the structure and activity of VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>142</sup> More specifically, P modification decreased the degree of VO<sub>x</sub> polymerization, which had positive implications on the catalyst stability, as evidenced by the retention of high activity (*ca.* 45% propane conversion) after an 8 h DDH reaction in all P-modified catalysts. This was almost twice the conversion reached with the unmodified catalyst. The combined and synergistic effect of the surface acidity modifications, their influence on the active V<sup>3+</sup> species, and weakened metal-support interactions facilitated desorption of propene and inhibited the deep dehydrogenation that leads to coke precursors.

Subsequent studies on a VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts (with 12 wt% V loading) modified with Mg revealed the anti-coking capability and improved catalytic performance evident through propene yields of 19–27% over a 6 h DDH reaction.<sup>143</sup> It was found that the dispersing action of Mg modification to V<sub>2</sub>O<sub>5</sub> crystallites and an increase in active V<sup>3+</sup> species reduced the amount and polymerization of coke deposits. However, the acidity decreases sharply with excessive Mg addition (above 1 wt%) as the excess MgO covers the surface VO<sub>x</sub> species, which leads to the loss of DDH activity. The highest STY achieved was 7.8 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sup>-1</sup><sub>cat</sub> h<sup>-1</sup> (Table 6, entry 7).

In addition to alumina, other supports have been investigated. Earlier reports by Ovsitser *et al.* described a silica supported VO<sub>x</sub> catalyst which exhibited high propene yield (86%), high stability and minimal deactivation over a 20 h DDH reaction.<sup>144</sup> Hu *et al.* explored vanadium doped porous silica (V-SiO<sub>2</sub>) with varying V : Si mass ratios of vanadium to silicon of 1 : 24, 1 : 12, 1 : 6, and 1 : 3, respectively.<sup>145</sup> The V/SiO<sub>2</sub> catalyst (with mass ratio of 1 : 12) displayed the optimal catalytic performance, achieving a superior initial propene yield of 59.5% and a stable propene selectivity of ~90% over 6 h at 580 °C. This was equivalent to a STY of 7.9 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sup>-1</sup><sub>cat</sub> h<sup>-1</sup> (Table 6, entry 4). Results from successive dehydrogenation-regeneration cycles indicated that the catalyst reached a stable

state displaying excellent regeneration stability after two dehydrogenation cycles. In common with VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts, moderate V loadings were concomitant with increased activity, which was attributed to more vanadium active sites in the channels of the porous silica with increased doping. The moderate vanadium doping level was conducive to highly dispersed vanadium species in the form of isolated and low-polymerized VO<sub>x</sub> species.

As previously discussed for other DDH catalysts, innovative techniques have also been applied in the preparation of V/SiO<sub>2</sub> catalysts. Vanadium-containing dendritic mesoporous silica nanoparticles (V-DMSNs) exhibited an initial propane conversion and propene selectivity of 18.1% and 91% respectively. The STY was calculated to be 22 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sup>-1</sup><sub>cat</sub> h<sup>-1</sup> (Table 6, entry 8), which is one of the highest VO<sub>x</sub> containing catalysts reported to date.<sup>146</sup> Compared to analogous catalysts synthesized *via* wet impregnation, the direct co-assembly process for the V-DMSNs catalysts contributed to enhancing the interaction between the V<sup>5+</sup> species and the silica support. Highly dispersed and stable VO<sub>x</sub> species, and an absence of V<sub>2</sub>O<sub>5</sub> crystallites, were conducive to high catalytic activity and stability. When tested for both ODH-O<sub>2</sub> and DDH reactions, the V-DMSNs catalysts displayed superior performance, signifying the importance of the preparation conditions and synthesis strategy to form well-defined structure of the support and sufficient concentration of highly dispersed and isolated VO<sub>4</sub> active sites.

Hu *et al.* investigated the influence of gelation and calcination temperatures on the properties and catalytic performance.<sup>147</sup> Interestingly, enhancement to catalytic performance in terms of propane conversion, propene selectivity and yield of propene were observed for VO<sub>x</sub>/SiO<sub>2</sub> catalysts (gelation temperature: 60 °C, calcination temperature: 580 °C). The VO<sub>x</sub>/SiO<sub>2</sub> catalyst exhibited an initial propane conversion of 55% and stable propene selectivity of *ca.* 91% over 4 h, with excellent reusability displayed over eight successive reaction-regeneration cycles. The STY was 6.2 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sup>-1</sup><sub>cat</sub> h<sup>-1</sup> (Table 6, entry 5), due to the low GHSV so while the catalyst achieved high selectivity at reasonable propane conversion, it was not as intrinsically active as other supported VO<sub>x</sub> catalysts.

Dealuminated beta zeolites (Si-beta) are promising catalyst supports due to their high surface area and thermal stability as mentioned before. Chen *et al.* synthesized numerous VO<sub>x</sub>/Si-beta zeolites with various V loadings (in the 0.5–10 wt% range) with the initial propane conversion shown to linearly increase with the amount of acid sites, Fig. 6.<sup>148</sup> This demonstrated the dependency of catalytic activity on total Lewis and Brønsted acid sites generated by VO<sub>x</sub> on silica, with Brønsted acid sites disappearing after high temperature treatment due to decomposition of hydrated VO<sub>x</sub>. The most active catalyst, V/Si-beta (having 3 wt% V loading) displayed an initial propene yield of 33.4% and retained activity over multiple dehydrogenation-regeneration cycles. Thus, only weak and medium strength sites were generated and ascribed to mono- and polymeric VO<sub>x</sub> species, respectively, both of which aided the adsorption and activation of propane. A correlation between



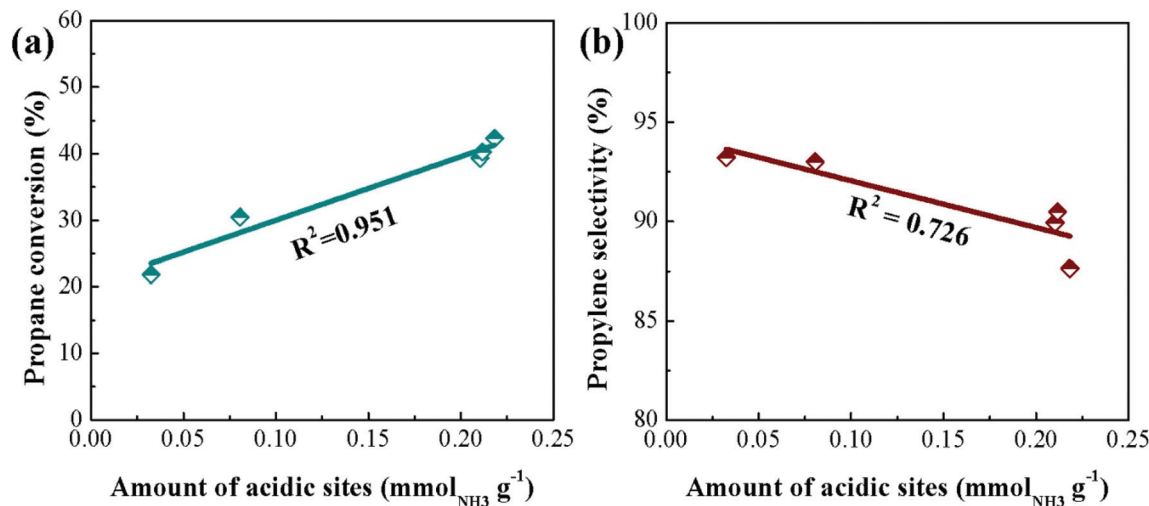


Fig. 6 Correlations between the (A) initial propane conversion and (B) propene selectivity as a function of the total amount of acidic sites, created by the interaction sites between V species and Si-Beta support in V/SiBeta catalysts. Reproduced from ref. 148 with permission from Elsevier.

increasing V loading, increased degree of polymerization and a subsequent increase in strong surface acid sites was reported. At 7 wt%  $\text{VO}_x/\text{Si-beta}$ , the STY was  $4.4 \text{ mol}_{\text{C}_3\text{H}_6} \text{kg}^{-1}_{\text{cat}} \text{h}^{-1}$  (Table 6, entry 6), which is 5–6 times less active than the most active  $\text{VO}_x$  catalysts reported to date, suggesting that Si-beta does not facilitate a high concentration of active V sites.

Alternatively,  $\text{ZrO}_2$  can be used as a support for  $\text{VO}_x$ . It was found that  $\text{VO}_x/\text{ZrO}_2$  is approximately five times more active than  $\text{VO}_x/\text{Al}_2\text{O}_3$  and pure  $\text{ZrO}_2$ , exhibiting a STY of  $9.2 \text{ mol}_{\text{C}_3\text{H}_6} \text{kg}^{-1}_{\text{cat}} \text{h}^{-1}$  (Table 6, entry 2).<sup>149</sup> The authors proposed that the enhanced performance of  $\text{VO}_x/\text{ZrO}_2$  results from the facile reduction of  $\text{V}=\text{O}$ ,  $\text{V}-\text{O}-\text{V}$  and  $\text{V}-\text{O}-\text{Zr}$  bonds, thus producing higher proportions of the active  $\text{V}^{3+}$  species. In view of this, Jeon *et al.* investigated various loadings of V on  $\text{VO}_x/\text{ZrO}_2$  catalysts.<sup>150</sup> For the most active catalyst, with 8 wt% V loading, the initial yield of propene increased from 24% at 550 °C to 28% at 575 °C with a negligible (<1%) increase at 600 °C. This corresponded to a STY of  $24 \text{ mol}_{\text{C}_3\text{H}_6} \text{kg}^{-1}_{\text{cat}} \text{h}^{-1}$  (Table 6, entry 3), which is one of the most active  $\text{VO}_x$ -based catalysts reported. As discussed later in section 4.5,  $\text{ZrO}_2$  is active by itself and therefore this result likely reflects the contribution from an active  $\text{ZrO}_2$  support rather than an optimised or improved  $\text{VO}_x$  catalyst. Indeed, the authors alluded to a correlation between activity and the formation of a higher concentration of coordinatively unsaturated ( $\text{Zr}_{\text{cus}}$ ) sites, created by the addition of the V dopant into the Zr lattice, increasing the density of Lewis acid sites. As discussed below, the STY of  $\text{ZrO}_2$  without  $\text{VO}_x$  is actually much higher than in the current work.

To date, many studies have investigated  $\text{VO}_x$ -based catalysts, which in some cases have been said to exhibit a catalyst performance similar to that of Pt- and  $\text{CrO}_x$ -based catalysts. However, comparing the typical STY values for  $\text{VO}_x$  with those of  $\text{CrO}_x$  or Pt, it is clear that the  $\text{VO}_x$  catalysts reported in the literature are not as active as supported  $\text{CrO}_x$  or Pt catalysts. In view of catalyst design, the nature of the support is an essen-

tial consideration, due to the importance of metal-support interactions and the influence of acid sites on the formation of different surface  $\text{VO}_x$  species. Of particular importance is the role of the support in altering stabilization and electronic effects of the active sites. Much like the industrial (Pt- and Cr-based) catalysts, the surface acidity and selectivity of the catalyst is affected by the nature of the support. Although the most active V species has been identified, the relative proportion and stability of this surface V species can be tuned by varying the preparation method. On the other hand, the role of the other V species on the DDH reaction remains unclear so further work to elucidate this could yield more active and stable DDH catalysts. The range in performance of V-based catalysts varies quite significantly, with the most active catalysts exhibiting STYs that are around 3–4 times less active than the most active Pt catalysts.

#### 4.5. Other DDH catalysts

As previously discussed, the industrial application of Pt- and  $\text{CrO}_x$ -catalysts is well established because they offer superior activity, selectivity and stability for the direct dehydrogenation of propane. However, these catalysts are limited in two main areas: economically, by the high cost of Pt and environmentally, by the toxicity of  $\text{Cr}^{6+}$  species. Thus, a definite need to develop alternative catalyst formulation exists.

Commonly, coordinatively unsaturated metal cations with neighbouring oxygen vacancies serve as adsorption sites for light alkanes, whereby surface oxygen sites abstract hydrogen from the adsorbed alkane. Armed with this knowledge, researchers continue to focus their efforts on catalyst design with the aim of enhancing dehydrogenation performance, creating both economic and environmental benefits.

Bulk  $\text{ZrO}_2$ , characterized with coordinatively unsaturated Zr cations ( $\text{Zr}_{\text{cus}}^{4+}$ ) as active sites, has emerged as a highly active and selective unsupported catalyst for the direct dehydrogena-



tion of propane. Kondratenko and co-workers first reported that  $\text{ZrO}_2$  is active in its own right for DDH and subsequently demonstrated the importance of crystallite size and phase composition in determining activity.<sup>151,152</sup> The rate of propene formation was inversely proportional to the crystallite size, but crucially, amorphous  $\text{ZrO}_2$  was very poorly active. Time on-stream conversions dropped significantly over time due to carbon deposition, but regenerative cycles were completed to examine if the activity could be regained. At 550 °C,  $\text{ZrO}_2$  was durable after 20 cycles but at 600 °C the  $\text{ZrO}_2$  crystallites sintered, causing a loss in activity. The initial performance corresponded to an STY of  $64 \text{ mol}_{\text{C}_3\text{H}_6} \text{ kg}^{-1}_{\text{cat}} \text{ h}^{-1}$  (Table 7, entry 13), which is one of the highest non-Pt values reported.

Jeon *et al.* reported the modification of  $\text{ZrO}_2$  with a vanadium dopant that exhibited an initial propene yield of 28%, excellent recyclability over ten cycles with no change in the active sites, and twice the activity observed in bulk undoped  $\text{ZrO}_2$ .<sup>150</sup> This was attributed to an increase in Lewis acidic ( $\text{Zr}_{\text{cus}}^{4+}$ ) active sites, that are a consequence of structural transformation. Additionally, the authors discovered that regardless of the vanadium content, all the catalysts exhibited a propene selectivity in excess of 98%.

Similarly, a positive effect from the modification of  $\text{ZrO}_2$  with a Cu dopant was reported by Jeon *et al.*<sup>153</sup> The optimal  $\text{CuZrO}_x$  catalyst displayed improved activity and selectivity at 600 °C compared to conventional (1 wt%)  $\text{Pt}/\text{Al}_2\text{O}_3$ , (0.5 wt% Pt-1.5 wt% Sn)  $\text{Pt-Sn}/\text{Al}_2\text{O}_3$  and (5 wt%  $\text{CrO}_x/\text{Al}_2\text{O}_3$ ). The authors established a correlation between the specific activity of  $\text{CuZrO}_x$  catalysts and the number of weak acid sites, resulting from the substitution of Cu in the Zr sub-lattice generating oxygen vacancies and  $\text{Zr}_{\text{cus}}^{4+}$  ions. The STY of the  $\text{CuZrO}_x$  catalyst was  $26 \text{ mol}_{\text{C}_3\text{H}_6} \text{ kg}^{-1}_{\text{cat}} \text{ h}^{-1}$ , compared to  $22 \text{ mol}_{\text{C}_3\text{H}_6} \text{ kg}^{-1}_{\text{cat}} \text{ h}^{-1}$  in the unmodified catalyst (Table 7, entries 9 and 10). While this improvement is promising, the STY was lower than half of an optimised  $\text{ZrO}_2$  catalyst previously reported in ref. 151, suggesting that there is still room for improvement in the  $\text{CuZrO}_x$  preparation, or that it is possible to promote activity through careful catalyst preparation rather than adding metals.

The concentration of dopant atoms, and the temperature of reduction were other contributing factors that affected the catalytic behaviour for  $\text{ZrO}_2$ -based catalysts.<sup>3</sup> Numerous binary  $\text{YZrO}_x$  and  $\text{LaZrO}_x$ -based catalysts displayed high activity, selectivity and stability as well as comparable performance to  $\text{K-CrO}_x/\text{Al}_2\text{O}_3$  catalysts over the course of 60 DDH cycles at 550 °C, 600 °C and 625 °C under industrially relevant conditions. The experimental parameters had a beneficial effect on the concentration of  $\text{Zr}_{\text{cus}}^{4+}$  ions, and the concentration of surface lattice oxygen, which in tandem play an active role in propane activation.

As discussed in the above sections, Zn has been used as a promotor in Cr and Pt catalysts. Sun *et al.* also investigated it as a promotor for Nb catalysts.<sup>154</sup> However, its use as a catalyst in its own right has recently been reported, notably by Yuan and co-workers. It was shown that ZnO nanoclusters supported in dealuminated zeolite-beta exhibited an initial propane conversion and propene selectivity of 53% and 97%, respectively at 600 °C. The initial STY was  $4.2 \text{ mol}_{\text{C}_3\text{H}_6} \text{ kg}^{-1}_{\text{cat}} \text{ h}^{-1}$ , and the conversion dropped to 40% after 6 h on-stream due to coking. ZnO/H-ZSM-5 was also investigated by the same group and it was shown that high  $\text{SiO}_2:\text{Al}_2\text{O}_3$  ratio supports yielded more selective DDH catalysts.<sup>155</sup> The presence of strong acid sites is known to promote coke formation *via* deep dehydrogenation and therefore this trend is expected. The highest STY yield was observed over 10 wt% ZnO/ZSM-5 where the  $\text{SiO}_2:\text{Al}_2\text{O}_3$  molar ratio was 280, which produced  $6.3 \text{ mol}_{\text{C}_3\text{H}_6} \text{ kg}^{-1}_{\text{cat}} \text{ h}^{-1}$  (Table 7, entry 12).

Kondratenko and co-workers reported the activity of ZnO supported on composites of N-doped carbon in silicalite-1.<sup>156</sup> Initial propane conversion and propene selectivity of the catalyst was *ca.* 52% and 89% respectively at. This corresponds to a STY of  $6.3 \text{ mol}_{\text{C}_3\text{H}_6} \text{ kg}^{-1}_{\text{cat}} \text{ h}^{-1}$  (Table 7, entry 11). Although the catalyst was active in the absence of the N-doped carbon composite, *i.e.* ZnO/silicalite-1, the activity was over 3 times lower. The role of the N-doped carbon was to encapsulate the ZnO nanoparticles and maintain high dispersion of the active component.

**Table 7** Catalytic performance of other selected catalysts for DDH reaction

Entry	Catalyst	T/°C	Feed composition	WHSV/ $\text{g}_{\text{C}_3\text{H}_8} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$	$X_{\text{C}_3\text{H}_8}/\%$	$S_{\text{C}_3\text{H}_6}/\%$	STY/ $\text{mol}_{\text{C}_3\text{H}_6} \text{ kg}^{-1}_{\text{cat}} \text{ h}^{-1}$	Ref.
1	$\text{Pd}_3\text{-Fe}$	510	$\text{C}_3\text{H}_8/\text{H}_2/\text{Ar} = 1.5 : 1.5 : 97$	8.0	22	87	32	165
2	$\text{Zn}/\text{ZrTiO}_x$	550	$\text{C}_3\text{H}_8/\text{H}_2/\text{N}_2 = 8 : 1 : 11$	4.7	30	95	55	157
3	OMC-2	600	$\text{C}_3\text{H}_8/\text{N}_2 = 1 : 19$	0.6	66	71	5.7	169
4	$\text{Co-Al}_2\text{O}_3$	590	$\text{C}_3\text{H}_8/\text{H}_2/\text{N}_2 = 1 : 0.8 : 3.2$	3.2	25	97	16	160
5	Sn-HMS	600	$\text{C}_3\text{H}_8/\text{C}_3\text{H}_6 = 99.87 : 0.13$	0.4	40	90	3.0	163
6	PT-MCN	600	$\text{C}_3\text{H}_8/\text{Ar} = 1 : 19$	0.6	33	85	3.4	171
7	CMSC <sub>700</sub>	600	$\text{C}_3\text{H}_8/\text{Ar} = 1 : 19$	0.6	41	89	4.5	168
8	$\text{Ni}_3\text{-Ga}/\text{Al}_2\text{O}_3$	600	$\text{C}_3\text{H}_8/\text{Ar} = 1 : 9$	2.4	13	94	6.1	166
9	$\text{ZrO}_2$	600	$\text{C}_3\text{H}_8/\text{Ar} = 1 : 7.5$	2.8	22	99	22	153
10	$\text{CuZrO}_x$	600	$\text{C}_3\text{H}_8/\text{Ar} = 1 : 7.5$	2.8	26	99	26	153
11	ZnO/CN-silicalite-1	600	$\text{C}_3\text{H}_8:\text{H}_2:\text{N}_2 = 1 : 1 : 5$	0.54	52	89	6.3	156
12	ZnO/H-ZSM-5	600	$\text{C}_3\text{H}_8/\text{Ar} = 19 : 1$	0.54	70	80	6.3	155
13	$\text{ZrO}_2$	600	$\text{C}_3\text{H}_8/\text{Ar} = 1 : 1.5$	11.7	28	86	64	151

T = reaction temperature; feed composition = molar ratio of  $\text{C}_3\text{H}_8/\text{H}_2/\text{carrier}$  in the reaction,  $X_{\text{C}_3\text{H}_8}$  = initial propane conversion,  $S_{\text{C}_3\text{H}_6}$  = initial propene selectivity, STY = space time yield.





While the above studies indicated that supported Zn catalysts can be selective DDH catalysts, the STY values were an order of magnitude below typical Pt and CrO<sub>x</sub> based catalysts. However, this gap in performance was recently closed by Han *et al.*, who investigated a range of Zr-containing metal oxides as supports for Zn, including ZrO<sub>2</sub>, TiZrO<sub>x</sub> and CeZrO<sub>x</sub> (as well as control catalysts without ZrO<sub>2</sub> such as Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>).<sup>157</sup> High catalyst activity was observed when Zr was present in the support, which is expected given that it is active by itself.<sup>151</sup> However, the origin of the high activity could also be linked to the speciation of Zn. In the most active catalyst, 4 wt% Zn/TiZrO<sub>x</sub>, the Zn was present exclusively as isolated tri-coordinated Zn<sup>2+</sup>O<sub>x</sub>. This catalyst produced a STY of 55 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sup>-1</sup><sub>cat</sub> h<sup>-1</sup> at 550 °C (Table 7, entry 2). Long term stability studies over 250 h and 10 regeneration cycles showed that a small drop in propane conversion and no loss in propene selectivity takes place. The drop in propane conversion was confirmed by ICP analysis to be due to loss of Zn from the catalyst. Temporal analysis of products studies were carried out to probe the rate-determining step of the reaction over supported Zn catalysts. Interestingly, it was shown that the formation of H<sub>2</sub> was rate-limiting in the catalyst, not C–H bond activation. Additionally, the presence of Ti in the catalyst support was shown to promote H<sub>2</sub> formation, which suggests that Ti in general is a good choice for a propane dehydrogenation catalyst. The observation that Zn–Zr catalysed DDH is not limited by C–H bond activation is a significant finding. As observed over similar catalysts, the rate of coke formation was dependent on acid and base sites, in this case present on the support. However, the best predictor of coke formation rate was the number of basic sites on the catalyst, which showed a strong positive correlation.

In section 3, the current commercial processes for propane dehydrogenation were presented and discussed. With the exception of the K-PRO process by KBR, all of the commercial catalysts have been disclosed. It is only known that the catalyst does not consist of Pt or Cr. We note that a patent was filed in the US in 2020 by Mukherjee *et al.* at Exelus, inc. (who developed the catalyst that is licensed to the K-PRO process)<sup>158</sup> for alkane dehydrogenation using a catalyst consisting of Zn, Zr and Ti oxides.<sup>159</sup> The optimal loadings and formulations disclosed in the patent are very similar to those reported by Han *et al.*<sup>157</sup> and therefore we tentatively suggest that the catalyst in the K-PRO process is likely to be based on Zn–Zr–Ti–O<sub>x</sub>.

Co-Based catalysts have also been demonstrated as potential alternatives to Pt- and Cr-based catalysts. Dai *et al.* reported a Co/Al<sub>2</sub>O<sub>3</sub> catalyst with a high stability and selectivity (>97% propene selectivity), and a corresponding STY of 16 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sup>-1</sup><sub>cat</sub> h<sup>-1</sup> (Table 7, entry 4).<sup>160</sup> Through extensive characterization it was observed that the Al<sub>2</sub>O<sub>3</sub> sufficiently stabilized isolated Co<sub>2</sub><sup>+</sup>, preventing surface reconstruction of Co species under reaction conditions. As a result, the catalyst efficiently facilitated propene desorption, inhibiting the formation of coke and other by-products. The application of a reductive-reoxidation treatment positively affected dehydrogenation performance of Co/Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>161</sup> An initial

propene yield of 28% and high selectivity to propene (>93%) was obtained over the course of the reaction. The authors attributed this to increased dispersion of Co metal species, a consequence of the mild reoxidation conditions resulting in markedly smaller (6 nm) Co metal nanoparticles, contrary to those observed in the fresh (34 nm) and reduced counterparts (25 nm).

As an efficient promoter of Pt-based catalysts, Sn was previously thought to be an inactive metal for dehydrogenation reactions. Surprisingly, metallic Sn supported on SiO<sub>2</sub> has proven to be an efficient, dehydrogenation catalyst, exhibiting a sustained propene yield of 30% over the course of a 70 h DDH reaction at 600 °C.<sup>162</sup> The incorporation of a hydrogenation component (Pd) can improve the stability of this catalyst, however, loss of Sn metal under reaction conditions, as a consequence of its low melting point, requires further investigation into more suitable supports than SiO<sub>2</sub>. Hexagonal mesoporous silicas have emerged as possible candidates due to Sn-HMS exhibiting high propane conversion (*ca.* 40%) and enhanced stability after multiple oxidative regenerations and 170 h on-stream.<sup>163</sup> The improved stabilization is a result of two factors: firstly, Sn incorporation into the lattice of HMS forms strong Sn–O–Si bonds, which inhibit Sn reduction to low melting point Sn<sup>0</sup>, and secondly, additional stabilization of the Sn species is induced by the mesoporous structure of the HMS support.

Wang *et al.* revealed the dependency of the nature and distribution of SnO<sub>x</sub> species on the Sn loading, and through advanced characterization revealed uniform distribution and stabilization of isolated Sn<sup>4+</sup> species in fresh samples, whilst being stabilized in the Sn<sup>2+</sup> state after reduction on SiO<sub>2</sub> due to strong metal–support interactions.<sup>164</sup> Superior long-term stability, as well as recovery of the initial activity upon oxidative regeneration, suggests that these materials could be very promising DDH catalysts.

Pd and Pd<sub>3</sub>–Fe supported on SiO<sub>2</sub> exhibited propene yields of 4.5% and 9.4% respectively at 510 °C. The bimetallic catalyst exhibited a much higher propene yield than Pd-only, despite both catalysts having a similar average nanoparticle size (*ca.* 2 nm).<sup>165</sup> The STY of the Pd<sub>3</sub>–Fe catalysts was 32 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sup>-1</sup><sub>cat</sub> h<sup>-1</sup> (Table 7, entry 1). This was partly due to a geometric effect in the formation of the Pd<sub>3</sub>–Fe alloy nanoparticles, breaking the ensemble of Pd, thus enhancing the selectivity and suppressing structure sensitive C–C hydrogenolysis and coking reactions. Electronic effects, often thought to promote high selectivity in Pt dehydrogenation catalysts, were not concluded to strongly influence the selectivity of Pd<sub>3</sub>–Fe/SiO<sub>2</sub>.

Recent advances in catalyst design have yielded non-noble-based intermetallic compound (IMC) catalysts, which present unique surface and catalytic chemistry that may be promising for propene production. He *et al.* explored highly selective and stable phase-pure Ni<sub>3</sub>–Ga IMC nanoparticles with Ga-rich surfaces supported on Al<sub>2</sub>O<sub>3</sub>. These exhibited high selectivity (~94%), good stability over long term (82 h) testing and regeneration ability at 600 °C, resulting in a STY of 6.1 mol<sub>C<sub>3</sub>H<sub>6</sub></sub>



$\text{kg}^{-1}_{\text{cat}} \text{h}^{-1}$  (Table 7, entry 8).<sup>166</sup> In order to compare with industrial-type catalysts, Pt-Sn/ $\text{Al}_2\text{O}_3$  (Oleflex) and  $\text{CrO}_x/\text{Al}_2\text{O}_3$  (CATOFIN) catalysts were prepared and tested under the same reaction conditions. It was shown that the  $\text{Ni}_3\text{-Ga}/\text{Al}_2\text{O}_3$  catalyst exhibited comparable conversion to Pt-Sn/ $\text{Al}_2\text{O}_3$  and inferior conversion to  $\text{CrO}_x/\text{Al}_2\text{O}_3$ , although after 14 h on-stream the  $\text{CrO}_x/\text{Al}_2\text{O}_3$  had deactivated to a similar conversion as  $\text{Ni}_3\text{-Ga}/\text{Al}_2\text{O}_3$ . Although the authors claim that  $\text{Ni}_3\text{-Ga}/\text{Al}_2\text{O}_3$  exhibited comparable performance to the commercial catalysts, there is no indication that the Pt-Sn/ $\text{Al}_2\text{O}_3$  and  $\text{CrO}_x/\text{Al}_2\text{O}_3$  catalysts prepared in this work would be as active as the actual commercial catalysts. Furthermore, the STY of all of the catalysts was an order of magnitude below the literature values associated with Pt-Sn and  $\text{CrO}_x$  catalysts (Tables 3 and 4, respectively).

Typically, oxygenic functional groups on the surface of carbonaceous materials, high surface area, stable structure, tuneable nanoscale dimensions and porosity are all important parameters which determine the efficiency of metal free carbon-based dehydrogenation catalysts. The induced activity of the oxygenic functional groups is a consequence of localization of  $\pi$ -electrons from defects, edges and vacancies.<sup>167</sup> Meanwhile, their porous structures are key determinants in achieving efficient mass and diffusion transfer.

Hu *et al.* recently reported the exploitation of biomass-derived porous carbon materials as dehydrogenation catalysts prepared by a simple alkali (KOH) activation method.<sup>168</sup> The carbon catalyst activated with KOH at 700 °C exhibited the best catalytic activity, displaying an initial propene yield of 36.6% and a STY of  $4.5 \text{ mol}_{\text{C}_3\text{H}_6} \text{kg}^{-1}_{\text{cat}} \text{h}^{-1}$  (Table 7, entry 7). The activity was attributed to the carbon catalysts possessing high surface area, hierarchical porous structure, and abundant oxygenated functional groups. Interestingly, no carbon deposition was observed with a carbon balance of 100% being maintained over 10 h of reaction time, rendering high stability signified by negligible loss in surface area and pore volume.

Recent interest into mesoporous carbons has yielded numerous dehydrogenation catalysts, with the large and well-ordered porosity proving beneficial for mass transport while long term stability (of up to 100 h) has also been shown, which exhibited an STY of  $5.7 \text{ mol}_{\text{C}_3\text{H}_6} \text{kg}^{-1}_{\text{cat}} \text{h}^{-1}$  (Table 7, entry 3).<sup>169</sup> As discussed above, it has been previously mentioned that coke formed in the DDH reaction can catalyse the reaction itself, so it is expected that carbonaceous catalysts would exhibit some activity. Of course the obvious drawback of such catalysts is the inability to burn off the coke, as would be typically done over mixed metal oxide or supported Pt catalysts in order to regenerate them. Mesoporous carbons prepared *via* a soft templating method and carbonized at 600 °C, 700 °C and 800 °C were investigated by Hu *et al.*<sup>170</sup> The increase in carbonization temperature positively influenced the propene selectivity of the aforementioned catalysts to 85.6%, 88.7% and 93.5%, respectively. The authors observed tuneable concentrations of the C=O, O=C-O and -OH functional groups by adjusting the carbonization temperature. As such, low carbonization temperatures (600 °C) enhanced deep cracking due to

surface acidic sites (*e.g.* O=C-O), hindering propene desorption. The subsequent increase in carbonization temperature (up to 700–800 °C) caused the decomposition of the acidic sites, thus increasing propene selectivity. Consequently, a linear relationship between the concentration of C=O groups and specific activity was established. The application of resorcinol-formaldehyde and Pluronic F127 also induced different pore ordering, with highly ordered mesoporous carbons displaying improved catalytic performance as a result of more accessible active sites and favourable mass transport properties.

Moreover, Pan *et al.* reported the modification of carbon with phosphorus from various sources, which introduced defects, forming numerous surface functional groups.<sup>171</sup> It was found that P modification of mesoporous carbon with triethyl phosphate had a promoting effect relative to  $(\text{NH}_4)_2\text{HPO}_4$ - and  $\text{H}_3\text{PO}_4$ -modified mesoporous carbon displaying initial propene yields of 27.2%, 18.7% and 17.2%, respectively. The most active catalyst exhibited a STY of  $3.4 \text{ mol}_{\text{C}_3\text{H}_6} \text{kg}^{-1}_{\text{cat}} \text{h}^{-1}$  (Table 7, entry 6). The improved catalyst performance was attributed to larger specific surface area, pore volumes, and pore sizes, as well as an increased number of carbonyl/quinone groups and a higher degree of graphitization.

There are many non Pt, Cr, Ga and V containing catalysts in the literature that have not been given the same attention as the aforementioned elements. Notable examples include Zn/ZrTiO<sub>x</sub> and ZrO<sub>2</sub>, which in terms of STY, outperform many Pt and Cr-based catalysts. These catalysts consist of non-toxic, abundant elements and are good candidates for commercialisation. Based on an analysis of the patent literature and commercial press releases, we suggest that the catalyst in the K-PRO process consists of a mixed metal oxide of Zr, Zn and Ti. Despite very impressive catalyst performance, investigations into Zn and Zr catalysts are very few. In contrast to Pt, Cr, Ga and V catalysts, which have been extensively studied and are fairly well-understood, Zn and Zr catalysts should be studied in greater detail to better understand the active species involved and how the performance can be further improved.

In conclusion, the direct dehydrogenation of propane can be catalysed by a broad range of metal oxides. Pt and Cr-based catalysts constitute the most commonly reported catalysts and are amongst the most active, which is not surprising given that both of these have been implemented in commercial processes. However, improvements in this sub-field of catalyst research has been incremental for some time and it is unlikely that a step-change in activity will be realised by further investigation. In contrast, Zr and Zn based catalysts are relatively immature and there are many opportunities to prepare highly active, stable DDH catalysts using these elements. Despite numerous investigations into coke formation over various catalysts, all DDH catalysts are prone to coking to some extent, and this remains the frontier in DDH catalyst design. More often than not, the origin of coke formation is due to strong acid/base sites on the support, or specific structures of the active component. Careful preparations and appropriate promoters can help to neutralise coke formation, but this can come at the expense of propene selectivity or propane conversion.



## 5. Oxidative dehydrogenation with oxygen

The oxidative dehydrogenation of propane using oxygen (ODH-O<sub>2</sub>) is an attractive route to propene due to favourable thermodynamics, theoretically being unlimited and exothermic is highly beneficial for industrial scale-up. Oxygen is cheap and non-toxic, but conditions must be controlled to ensure that the oxygen/propane ratio is not flammable. Regarding safety and industrially relevant processes, if selectivity is improved further for ODH-O<sub>2</sub>, then the reaction could be an exciting and useful process. In general, productivities are not currently high enough to be of interest for industrial application due to the low selectivity of many metal oxide catalysts, but more recent developments in the field may change this, with boron-based catalysts forming ethene as a secondary product in contrast to CO<sub>x</sub> products over metal oxide catalysts.

ODH-O<sub>2</sub> reaction pathways are much simpler than DDH and ODH-CO<sub>2</sub>, with fewer side reactions and products forming over typical catalysts. Overoxidation is the main limitation in ODH-O<sub>2</sub>. For metal oxide-based catalysts, gaseous oxygen is utilised *via* a Mars-Van Krevelen mechanism, with lattice oxygen abstracting hydrogen from propane. The following section describes the most significant literature reports on catalysts for ODH-O<sub>2</sub>.

### 5.1. Vanadia based ODH-O<sub>2</sub> catalysts

The first vanadia-based catalysts for oxidative dehydrogenation were V-Mg-O catalysts applied for the ODH-O<sub>2</sub> of butane. In 1988, V-Mg-O catalysts were found to be active and selective to propene when compared to V<sub>2</sub>O<sub>5</sub> and MgO.<sup>172</sup> Since this early discovery, there have been many investigations into V-based catalysts for ODH-O<sub>2</sub>, which have focussed on catalyst optimisation as well as understanding the nature of the active site.

Sam *et al.*<sup>173</sup> analysed Mg<sub>2</sub>V<sub>2</sub>O<sub>7</sub>, which in contrast to other V-Mg-O phases tested, contained vanadium species with a V=O bond. Mg<sub>2</sub>V<sub>2</sub>O<sub>7</sub> exhibited a conversion of 6.9% and propene selectivity of 53.5% at 550 °C, which was much more productive than Mg<sub>2</sub>V<sub>2</sub>O<sub>8</sub> and Mg<sub>2</sub>V<sub>2</sub>O<sub>6</sub>. This early work highlighted the importance of the V=O bond in producing effective ODH-O<sub>2</sub> catalysts. Corma *et al.* later examined the influence of supports for supported vanadia catalysts.<sup>174</sup> It was shown that VO<sup>2+</sup> pairs present in V<sub>2</sub>O<sub>5</sub> are active for ODH-O<sub>2</sub> but were also the source of overoxidation to CO<sub>x</sub> products. More acidic supports, such as silica, decreased dispersion and therefore more V<sub>2</sub>O<sub>5</sub> was detected, compared to more basic supports such as MgO and TiO<sub>2</sub>. It was also found that if the V=O bonds were adjacent to V-O sites, then overoxidation occurred. Limiting the formation of V<sub>2</sub>O<sub>5</sub> and forming V-O sites with tetrahedral coordination was found to be crucial to forming a selective catalyst.

Subsequent reviews of the literature by Kung and Kung,<sup>175</sup> and Blasco and López Nieto<sup>176</sup> further highlighted that V=O bonds were the active sites for ODH-O<sub>2</sub> in these materials. These reviews have guided modern investigations to focus on

preparing isolated V species on metal oxide supports, rather than Mg-containing mixed oxide materials. It was shown that ODH-O<sub>2</sub> rates initially increase with VO<sub>x</sub> surface density but decrease when V<sub>2</sub>O<sub>5</sub> crystallites form at high V loadings, due to agglomeration of particles. It was also found that the formation of V<sub>2</sub>O<sub>5</sub> crystallites significantly reduced the selectivity to propene, as the surface propyl species will react over two V atoms.<sup>177</sup> The formation of V<sub>2</sub>O<sub>5</sub> was shown to occur at lower V loadings for more acidic supports, such as SiO<sub>2</sub>, whilst using a high surface area silicate, MCM-41, was found to maintain a high STY due to a larger area for dispersion.<sup>178</sup> A general trend can be shown across the literature in which isolated VO<sub>4</sub> species (sometimes denoted as monomolecular or monomeric) are predominant at low vanadium loadings, and as the VO<sub>x</sub> surface density increases, the predominant V species become V<sub>2</sub>O<sub>7</sub> dimers, forming polymeric vanadia across the surface (also commonly denoted in the literature as polyvanadate, V<sub>2</sub>O<sub>5</sub>-like, 2-dimensional or more generally, VO<sub>x</sub>). With higher V loadings, V<sub>2</sub>O<sub>5</sub> crystallites become present (also denoted as 3-dimensional species), as shown in Fig. 7. This has been shown to be the case for many supports including SBA-15,<sup>179</sup> TiO<sub>2</sub><sup>180</sup> and γ-Al<sub>2</sub>O<sub>3</sub>.<sup>181</sup>

The density of isolated V sites can also be influenced by the nature of the support, and some supports can sustain a higher density of isolated V sites compared to others. For example, a higher density of isolated V sites was achieved on SBA-15, when compared to conventional SiO<sub>2</sub> and MCM-41, due to a lower surface acidity.<sup>183</sup> The loading of vanadia required to sustain only monomeric sites is 8–9 V nm<sup>−2</sup> on most supports, with SiO<sub>2</sub> showing a maximum loading of 3.3 V nm<sup>−2</sup> for monomer only coverage.<sup>184</sup> SiO<sub>2</sub> tends to have a poor interaction with the vanadia precursor species in general due to similarities in the acidity of both, so dispersion of V atoms is lower. Depending on the preparation method, monomolecular or polymeric species can exist with high dispersion, or 3-dimensional V<sub>2</sub>O<sub>5</sub> crystallites can form even below monolayer coverage.

An in-depth review of vanadia based catalysts for ODH-O<sub>2</sub> was undertaken by Carrero *et al.*<sup>4</sup> in 2014. The review highlighted that the activity of supported vanadia catalysts can be explained by one scaling parameter: the energy of oxygen defect formation. This in turns defines the reducibility of the site and therefore the redox potential. In practice, the formulation of the oxide support, the V loading (and subsequently, the dispersion and speciation) all affect the final catalyst structure and give rise to the wide-range of performances reported. The review also highlighted the complexity in the relationship between V species and catalytic activity: not all VO<sub>4</sub> units are equally active; the local geometry and support affect the reducibility and therefore activity. In fact, the authors concluded that despite many reports in advancing the synthesis of supported VO<sub>x</sub> catalysts, only a minority of surface species are highly active. Since 2014, several studies have further improved vanadia dispersion and subsequently, the catalyst performance. The most significant advances in this endeavour are discussed below.



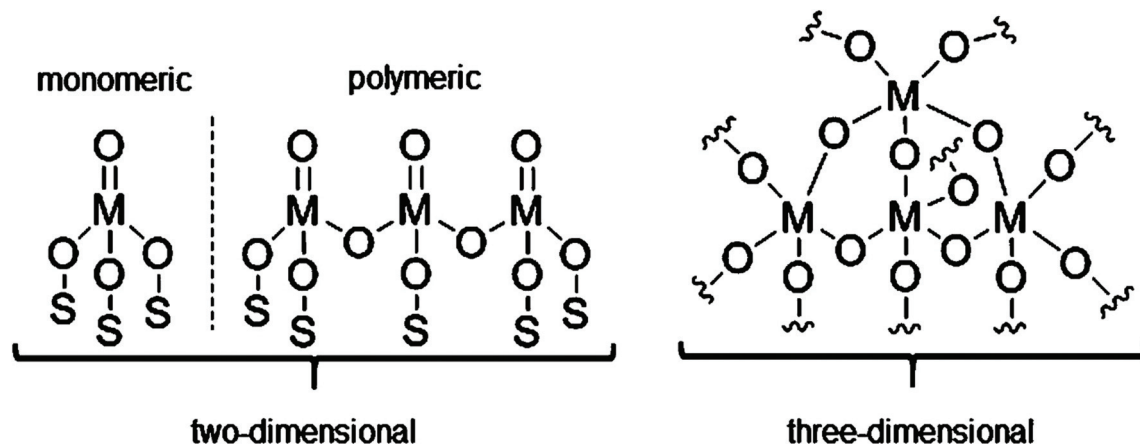


Fig. 7 Two dimensional (monomeric and polymeric) and three-dimensional structures for supported metal catalysts. S = support atom, M = support metal.<sup>182</sup>

The use of acidic supports has been probed, as acidity has been shown to increase the activity of ODH- $O_2$  catalysts. Supporting  $VO_x$  supported on H-ZSM-5 was shown not to enhance performance since, despite the acidity of the support increasing propane conversion for low V loadings. The support influence was detrimental to selectivity and overall lowered the propene yield. The isolated  $VO_x$  species present at low V loadings became reduced at a lower temperature compared to polyvanadate species and  $V_2O_5$ , suggesting that isolated species can facilitate oxidation of propane more effectively.<sup>185</sup>

In contrast, vanadia has been supported on  $Al_2O_3$  that was doped with varying concentrations of MgO to induce basic site functionality.<sup>186</sup> Increasing the Mg content led to a decrease in strong acid sites, decreasing activity, consistent with the fact that strong acid sites can activate propene. An Mg/V ratio of 0.8 showed the highest yield of propene, as the ratio of Mg/V balanced the effects of strong acid sites for propane conversion, whilst limiting overoxidation through the addition of Mg resulting in a change of surface species and acidity. The strength of the V-O bond was also influenced by Mg doping, with the binding energy of V-O bonds increasing with increasing Mg content. This effect increased selectivity by decreasing overoxidation due to the inhibited lability of lattice oxygen.

Zhang and Liu<sup>187</sup> also investigated V-Mg-O catalysts with the aim of increasing the loading whilst maintaining a high level of dispersion on SBA-15, which has previously been shown to limit  $V_2O_5$  crystallite formation even at low loading levels. To limit agglomeration of vanadia, co-impregnation of V and Mg was undertaken which resulted in the suppression of 3D  $V_2O_5$  crystallite formation. In this investigation, it was shown that with increasing V content, the V environments went from isolated  $VO_4$  species to  $Mg_3V_2O_8$ , and no crystalline  $V_2O_5$  was detected, even with V loading levels of 25 wt% when using co-impregnation of V and Mg. The  $Mg_3V_2O_8$  phase was shown to be intrinsically more selective than dispersed  $VO_4$ , and at 20% propane conversion, propene selectivity was found to be higher for Mg-V-O catalysts, than V-O catalysts, with some

dependence on crystallite size (a 20–30 nm crystallite size gave the highest propene selectivity of ~59%). Small  $Mg_3V_2O_8$  crystallites showed preferential kinetics (*i.e.*, a higher rate of propene formation compared to rate of combustion and rate of propene formation) when compared with dispersed  $VO_4$  species, since the latter have an increased preference for propene oxidation compared to  $Mg_3V_2O_8$ . This is interesting as  $H_2$ -TPR showed a lower level of reducibility for  $Mg_3V_2O_8$  when compared to  $VO_4$  species, suggesting that former catalyst was sufficiently reducible to achieve oxidation of propane, but not to overoxidise to  $CO_x$  products.

Supporting vanadia on SBA-15 *via* wet impregnation has been explored and a loading of 6.6 wt% V achieved a surface density of  $1.6 \text{ V nm}^{-2}$ , the highest surface density achieved on SBA-15 without  $V_2O_5$  crystallite formation; coverage was increased by rehydrating the support before impregnation, aiding dispersion.<sup>188</sup> The increased dispersion led to an increased selectivity when compared to similar catalysts. Zhu *et al.* investigated pre-treatment of the support, with the simple idea that modifying the support before loading V could control the dispersion.<sup>189</sup> A  $SiO_2$  support was treated at different temperatures before grafting  $VOCl_3$  onto the surface. Higher temperature treatments (700 °C to 1000 °C) resulted in the removal of neighbouring silanols and only isolated silanols were detected using IR spectroscopy. Isolated silanols can anchor  $VO_x$  species, and isolated silanols would be expected to produce monomeric  $VO_4$ . Due to the silanol site concentration decreasing, the loading of vanadia decreased with increasing support pre-treatment temperature. However, the increase in pre-treatment temperature also led to an increase in monomeric vanadia sites compared to dimeric sites. The catalysts with the highest abundance of isolated monomers showed the highest propene selectivity of 90% at 500 °C and 68% at 600 °C (Table 8, entry 4), leading to the conclusion that monomeric sites are more selective than the polymeric structure. This study highlighted the difference in selectivity between different  $VO_x$  species. It must be noted that no 3D  $V_2O_5$  crystal-





**Table 8** Summary of catalytic performance of selected vanadia based ODH-O<sub>2</sub> catalysts

Entry	Catalyst	T/°C	O <sub>2</sub> /C <sub>3</sub> H <sub>8</sub>	WHSV/h <sup>-1</sup>	X <sub>C<sub>3</sub>H<sub>8</sub></sub> /%	S <sub>C<sub>3</sub>H<sub>6</sub></sub> /%	STY/mol <sub>C<sub>3</sub>H<sub>6</sub></sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	Ref.
1	5V-Zr-O fibres	400	0.5	70.8	4.0	64.6	38	192
2	0.4Na <sup>+</sup> -V-SiO <sub>2</sub>	490	0.5	19.3	6.5	66	17	182
3	3V/γ-Al <sub>2</sub> O <sub>3</sub>	500	0.5	4.7	12.5	75.9	9.4	194
4	VO <sub>x</sub> /SiO <sub>2</sub> -(1000)	500	1	4.7	30	60	18	189
5	3V-DMSN	500	0.5	6.3	10.4	66.5	9.1	146
6	V/SiO <sub>2</sub> (SOMC)	525	0.5	118	5	66	82	190
7	1.8V-KIT-6	550	1	4.7	46.2	64.5	30	193

T = reaction temperature O<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> = molar ratio of CO<sub>2</sub> : C<sub>3</sub>H<sub>8</sub> in the reaction, X<sub>C<sub>3</sub>H<sub>8</sub></sub> = initial propane conversion, S<sub>C<sub>3</sub>H<sub>6</sub></sub> = initial propene selectivity, STY = space time yield. Value next to element/phase represent wt%.

lites were detected when using VOCl<sub>3</sub> grafting on heat-treated SiO<sub>2</sub> supports, and therefore selectivity to propene was maintained.

To probe the influence of monomer sites, Barman *et al.*<sup>190</sup> grafted monomeric V species onto SiO<sub>2</sub> using surface organo-metallic chemistry (SOMC). This approach represents another example of changing the preparation technique to increase dispersion. It was found in this study that monomeric vanadia species are intrinsically more selective. The incipient-wetness impregnation technique formed catalysts which were more selective than SOMC catalysts below 500 °C, but above this temperature, the SOMC catalysts exhibited an equivalent or even higher selectivity. A STY of 82 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> (Table 8, entry 6) was measured over V/SiO<sub>2</sub> prepared *via* SOMC.

In addition to high dispersion and control of oxygen environments of the vanadia, tailored support properties are crucial in optimising ODH-CO<sub>2</sub> performance. A widely debated topic in catalysis is the effect of support porosity on catalytic properties. The preparation route of Al<sub>2</sub>O<sub>3</sub> was varied to form flower-like, sphere-like and bulk-like morphologies to investigate the influence of varying porosities. Bulk-like morphology only exhibited intraparticle pores, and the monolithic architecture of γ-Al<sub>2</sub>O<sub>3</sub> (formed by a roasting method) achieved the highest productivity for ODH-O<sub>2</sub>, despite the surface vanadia species being consistent across all architectures, with the degree of polymerisation being fairly similar for all Al<sub>2</sub>O<sub>3</sub> structures as (shown by adsorption edge energy analysis).<sup>191</sup> The bulk-like morphology showed a lower resistance to external mass transfer, and reduced the residence time of propene through the catalyst bed, lowering the tendency for further reactions.

Mesoporosity was also explored when forming fibrous vanadia catalysts *via* electrospinning. A comparison between fibrous catalysts which presented mesoporosity, and particle-like catalysts without apparent mesoporosity, indicated no influence on catalytic performance due to porosity,<sup>192</sup> consistent with the aforementioned morphology analysis. However, it is interesting to note that a change in preparation technique changed performance. A one-step synthesis to form VZrO<sub>x</sub> catalysts was found to form the most active catalyst with 5 wt% V loading, when compared to incipient wetness impregnation catalysts. Incipient wetness impregnation with 5 wt% V

loading showed the formation of 3D-V<sub>2</sub>O<sub>5</sub> crystals, known to be detrimental to selectivity, whilst the one-step process did not show evidence of V<sub>2</sub>O<sub>5</sub> formation and improved the dispersion of isolated VO<sub>x</sub> sites. It is also noteworthy that the VZrO<sub>x</sub> catalysts from the research by Ternero-Hidalgo *et al.* operate at a lower temperature, namely 400 °C, when compared to other catalysts in the field (Table 8, entry 1) and achieved a STY of 38 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>.

Vanadia supported on dendritic mesoporous silica nanoparticles (V-DMSN) was formed *via* a one-step synthesis as DMSN materials were found to have large pore volumes and a larger surface area than conventional mesoporous silica.<sup>146</sup> The one step synthesis, similar to the VZrO<sub>x</sub> catalysts discussed previously, led to higher dispersion and a higher stability of vanadia on the DMSN support when compared to incipient wetness impregnation (denoted V/DMSN). A surface V density of 0.55 V nm<sup>-2</sup> (2 wt% V), gave the highest STY of 9.1 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> (Table 8, entry 5). H<sub>2</sub>-TPR analysis revealed that the isolated V species were more reducible, which is a strong predictor of activity in ODH-O<sub>2</sub>.

Despite SiO<sub>2</sub> having a large surface area, and that many different types of silica supports having been tested, the low reactivity of silanol groups towards V precursors means that a relatively low loading of isolated V sites are reported. Doping the SiO<sub>2</sub> surface with 0.4 wt% Na<sup>+</sup> enhanced the V dispersion to a level corresponding to monolayer coverage (*i.e.*, 8.6 V nm<sup>-2</sup> for 6.2 wt% V loading) (Table 8, entry 2), which is equivalent to many other metal oxide supports.<sup>182</sup> It was hypothesised that Na<sup>+</sup> ions provide a source of Si-O-Na<sup>+</sup> surface species, which facilitate increased monomeric vanadia species, boosting the propane conversion. However, it should be noted that the intrinsic activity of the V/SiO<sub>2</sub> catalysts did not increase; the calculated TOFs were similar for V supported on promoted and unpromoted SiO<sub>2</sub>. Instead, the presence of Na<sup>+</sup> simply facilitated a greater density of isolated V sites. The activity of the Na<sup>+</sup> promoted V/SiO<sub>2</sub> was sustained for 4.5 days and post-reaction Raman spectroscopy showed no formation of 3D V<sub>2</sub>O<sub>5</sub> crystallites. This is an excellent example of doping having a beneficial effect. However, it is sometimes found that doping has deleterious effects on redox properties. For instance, doping with K<sup>+</sup> was found to decrease the selectivity and activity when compared to V-only supported catalysts.<sup>193</sup> When loaded onto KIT-6 supports, the V began to segregate



with the addition of  $K^+$  ions because  $VO_x$  and  $K^+$  have a strong interaction, which led to the formation of unselective  $K^+$  and V mixed phases such as potassium vanadate. The interaction between  $K^+$  and  $VO_x$  species decreased the reducibility of the catalyst. Interestingly,  $K^+$  incorporation led to an increase in the ethene to propane ratio, but the alkene yield was decreased overall. The incorporation of basic metal oxides should be done cautiously, as the benefit of enhanced propene desorption can be outweighed by the detrimental effects on the redox properties of the catalysts.

In conclusion, vanadia catalysts have been extensively investigated for ODH- $O_2$ , with the main focus being on maximising the number of isolated vanadia species, which is fundamental to increasing propene selectivity. A more precise view of vanadia species in recent studies has shown isolated vanadia sites to be more selective than polymeric species which contain V-O-V bridging bonds. Therefore, high activity is associated with high V dispersion. Acidic supports inherently decrease V dispersion, thus decreasing selectivity and overall productivity despite increasing activity. More frequently, there are reports of dispersion being influenced by the preparation technique, with grafting vanadia onto the support surface showing promise. However, a one-step synthesis of support and vanadia, in contrast to analogous surface impregnation catalysts, has been shown to improve catalyst productivity. The one-step synthesis method was shown to improve productivity for different support materials, morphologies and loadings when compared to analogous catalysts formed with more traditional surface loading techniques. Research into one-step synthesis methods is far from exhausted and shows considerable potential for further development. In contrast, incipient-wetness techniques can still be improved, with hydration of the surface or doping being effective strategies. Doping has been shown to influence the intrinsic reactivity of the active sites, but an increase in activity is usually accompanied by a decrease in selectivity. Increasing selectivity *via* dispersion techniques may be deemed a more promising route to improving catalytic performance. The choice of support material composition and chemical properties is more influential than morphology on overall catalytic performance; many studies comparing mesoporous catalysts with bulk-like morphologies found mesoporosity to have either a detrimental or negligible

effect on productivity. Porosity can, however, increase specific surface area and therefore support a higher loading of isolated vanadia sites.

## 5.2. Boron-based ODH- $O_2$ catalysts

Boron based catalysts are relatively new to the field of dehydrogenation catalysis. Hexagonal boron nitride (h-BN) has historically been used a catalyst diluent due to its high thermal stability under oxidative conditions. The 2-D structure of h-BN also allows for high thermal conductivity *via* efficient phonon transmission across the sheets of BN.<sup>195</sup> High thermal conductivity is appealing with regards to industrial application, as this limits the formation of hot spots, and selectivity becomes more controllable. The discovery that h-BN catalyses propane dehydrogenation was first reported in 2016<sup>196</sup> and since then there has been significant developments in the understanding of the active centres and reaction mechanisms. In the initial investigation, h-BN (Table 9 entry 8) was observed to catalyse ODH- $O_2$ , with similar activity to  $V/SiO_2$  catalysts. However, boron nitride nanotubes (BNNTs) displayed higher productivity, selectivity and yield than conventional  $V-SiO_2$  catalysts with the BNNT having a STY of 110 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> (Table 9, entry 1), which is ~7 times greater than the analogous  $V/SiO_2$  materials tested.<sup>196</sup> Fig. 8 illustrates this difference in performance. In contrast to supported  $VO_x$  catalysts that produce  $CO_x$ , the major by-product is typically ethene, which is of course more valuable than carbon oxides.

Such a different product distribution hints at a distinct reaction mechanism from other metal oxide ODH- $O_2$  catalysts, and investigations into the reaction mechanism have suggested as much. First order dependence on  $O_2$  partial pressure and second order dependence on propane partial pressure was noted by Grant *et al.*<sup>196</sup> It was also suggested that molecular oxygen forms an “armchair” from B to N at the platelet edges to form a B-O-O-N active site, but subsequent studies found catalysts without any N present were also highly active.

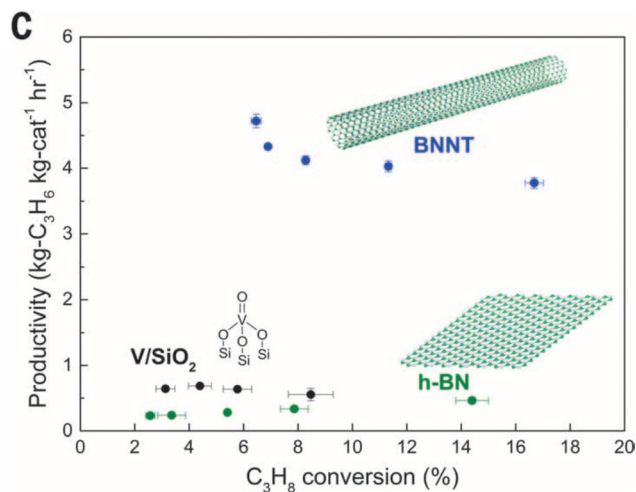
Edge-hydroxylated boron nitride (BN-OH) was subsequently reported to have the highest productivity of any previously reported catalyst for the dehydrogenation of propane.<sup>197</sup> BN-OH catalysts were also shown to be stable over 300 h on-stream (with no significant reduction or change in selectivity

**Table 9** Catalytic performance of selected boron-based catalysts for ODH- $O_2$

Entry	Catalyst	$T/^\circ\text{C}$	$O_2/C_3H_8$	WHSV/h <sup>-1</sup>	$X_{C_3H_8}/\%$	$S_{C_3H_6}/\%$	STY/mol <sub>C<sub>3</sub>H<sub>6</sub></sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	Ref.
1	BNNT	490	0.5	31.7	6.5	76	110	196
2	BN/DFNS	490	1	1.2	18	59.4	2.4	198
3	Elemental B	490	2	152.7	9.8	83	280	199
4	10B <sub>2</sub> O <sub>3</sub> /SBA-15	500	1.5	9.5	31.5	64	43	207
5	BN-OH	530	1.5	37.6	20.6	80.2	130	197
6	Macroporous BPO <sub>4</sub>	535	1.5	93.9	20.8	78.1	320	211
7	SiB <sub>6</sub>	545	1.5	9.5	31.1	72.1	48	201
8	h-BN	560	0.5	4.0	14	79	11	196

$T$  = reaction temperature;  $O_2/C_3H_8$  = molar ratio of  $O_2:C_3H_8$  in the reaction,  $X_{C_3H_8}$  = initial propane conversion,  $S_{C_3H_6}$  = initial propene selectivity, STY = space time yield. Values next to element/phase represent wt%.





**Fig. 8** Comparisons of propene productivity plotted as a function of  $C_3H_8$  conversion between  $V/SiO_2$ , h-BN, and BNNT.  $V/SiO_2$ : 5 to 15  $kg_{cat} s mol C_3H_8^{-1}$ ; h-BN: 15 to 40; BNNT: 2 to 5;  $T = 490^\circ C$ ,  $P_{O_2} = 0.15$  atm,  $P_{C_3H_8} = 0.3$  atm. Reproduced from ref. 196 with permission from The American Association for the Advancement of Science.

at  $530^\circ C$ ). The BN-OH materials were catalytically active after  $O_2$  activation, with DFT calculations suggesting that neighbouring B-OH sites formed B-O-B linkages once both B-OH groups are dehydrated. The sites could be reduced back to BN-OH using steam. Clear discrepancies were seen between previously proposed reaction mechanisms and explanations on how structure influences catalytic activity, showing that *in situ* edge functionalisation is key to catalytic activity. When comparing supported BN and supported  $B_2O_3$  on dendritic fibrous nanosilica (termed BN/DFNS and  $B_2O_3$ /DFNS respectively), BN/DFNS showed improved productivity relative to  $B_2O_3$ /DFNS, although both were active.<sup>198</sup> This finding is noteworthy, as it shows that BN on the surface can be oxidised to  $B_2O_3$  during the reaction. The as-prepared BN catalysts however already contained a large proportion of hydroxyl groups, underlining the importance of hydroxylated B in catalysing ODH- $O_2$ . This observation is consistent with the activity trends noted for edge-hydroxylated BN (Table 9, entry 2).

Subsequently, the Hermans group probed the influence of heteroatoms on activity and selectivity of boron-based catalysts using a range of metal borides, including  $B_4C$ ,  $TiB_2$ , elemental B (Table 9, entry 3) and WB amongst others. Elemental boron showed a remarkably high STY of  $280 mol_{C_3H_6} kg_{cat}^{-1} h^{-1}$ ,<sup>199</sup> which represented an improved productivity over BN-OH catalysts that had been previously described in the literature. In a subsequent review, it was noted that the propene selectivity was the same at isoconversion for every boron material that was tested,<sup>200</sup> suggesting that the boron heteroatom is the source of the active site. Metal borides with a high oxygen and boron surface content showed the highest productivities and the presence of  $BO_x$  species have been identified as essential for catalytic activity. The catalytic activity of various B compounds depended on the concentration of B at the surface.

Under ODH- $O_2$  conditions, the B is oxidised to  $BO_x$ , which is the active site. It was also shown that the activation of  $O_2$  is the rate-limiting step for boron-based catalysts in ODH- $O_2$ . These new insights disproved the previously suggested mechanism that required N.

Yan *et al.* reported that silicon boride was active for the oxidative dehydrogenation of propane, ethane and isobutane.<sup>201</sup> At  $545^\circ C$ ,  $SiB_6$  exhibited a STY of  $48 mol_{C_3H_6} kg_{cat}^{-1} h^{-1}$  (Table 9, entry 7) and subsequent stability tests at  $545^\circ C$  showed that a propane conversion of 20% and propene selectivity of 80% could be maintained over the 100 h experiment.

An extended literature review by Shi *et al.*<sup>5</sup> in 2018 outlined recent advances in testing and further understanding of structure–performance relationships. Key comparisons were drawn between traditional V catalysts and the highly promising B catalysts. In particular,  $CO_x$  selectivity for edge hydroxylated boron catalysts was shown to be 0.5%, in comparison to 10–50% for V-based catalysts, whilst productivities for boron catalysts can be maintained for 300 h. Mechanistic studies showed oxygen to have a reaction order of 0.5, suggesting that dissociative adsorption of oxygen is of importance to facilitate the reaction, whilst in the absence of oxygen catalysts had no activity. *In situ* infrared analysis has demonstrated that the presence of OH groups led to the interaction of molecular oxygen with the surface. Interestingly, alkane partial pressure was shown to have a reaction order of 2,<sup>197</sup> with two propane molecules needed during the reduction phase of the redox cycle, to form the two adjacent BN-OH sites in the original catalyst (Fig. 9).

As described above, there are differences in the reaction mechanism between boron-based catalysts when compared to supported metal oxide catalysts. For example, h-BN and other boron-based catalysts do not function for non-oxidative propane dehydrogenation,<sup>199</sup> whilst metal oxides do function initially and do not require an induction period. This shows that boron-based catalysts form the necessary active sites under reaction conditions, and that the initial catalysts can be perceived as precursors to the active phase. Propane partial pressures exhibit a second order rate dependence for h-BN, whereas in metal oxides it is first order. Metal oxide catalysts such as  $VO_x$  and  $MoO_x$  used for ODH- $O_2$  operate using *via* a Mars-Van Krevelen mechanism, whilst h-BN cannot do this due to the absence of lattice oxygen.<sup>200</sup> Therefore, in order to optimise boron-based catalysts, a more complete understanding of the reaction mechanism must be developed to tailor the nanostructure to the process.

DFT studies of optimised structures of h-BN have been undertaken to probe the ODH- $O_2$  reaction mechanism. The dissociative  $O_2$  adsorption was shown to be favoured on B terminated edges, rather than N terminated edges, leading to B atom terminated platelet edges being more active. DFT calculations also showed that the dehydrogenation reaction at B atom terminated edges is favoured over C–C bond breaking due to kinetic and thermodynamic factors.<sup>203</sup> Other DFT studies have built upon the understanding that boron is the active centre for ODH- $O_2$  and suggest that C–H abstraction is



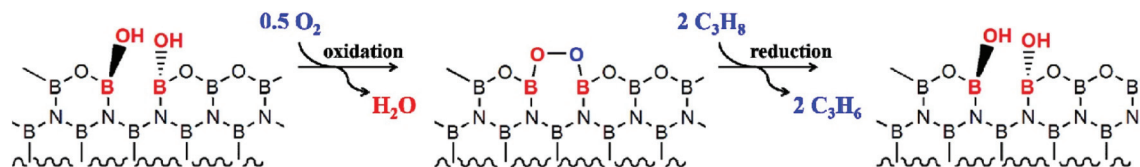


Fig. 9 Proposed reaction mechanism for ODH- $\text{O}_2$  over boron nitride catalysts for the oxidative dehydrogenation of propane. Reproduced from ref. 202 with permission from Elsevier.

undertaken by heterolytic cleavage over a B–O pair in a  $\text{BO}_3$  active structure. It has been suggested that  $\text{O}_2$  abstracts the hydrogen from the newly formed O–H group, reducing  $\text{O}_2$  to  $\text{HO}_2$ , and subsequently forms B–OOH and B– $\text{C}_3\text{H}_7$  on neighbouring  $\text{BO}_3$  sites. The  $\text{HO}_2$  group then abstracts hydrogen from the propyl surface intermediate to form propene, whilst  $\text{H}_2\text{O}_2$  breaks down to form  $\text{H}_2\text{O}$  and the  $\text{BO}_3$  active site is regenerated.<sup>204</sup>

Experimental studies comparing h-BN and  $\text{VO}_x/\text{Al}_2\text{O}_3$  once more highlighted the different reaction mechanisms at work. It has been shown h-BN exhibited a  $\text{C}_2/\text{C}_1$  product ratio of 2, whilst the  $\text{VO}_x$  catalyst shows almost no  $\text{C}_2$  products, and complete oxidation to  $\text{CO}_x$  dominated.<sup>205</sup> This implies that different reaction pathways dominate, with only the first C–C bond cleavage being favourable for h-BN catalysts, leaving the methyl group to have many different reaction pathways. Interestingly, an increase in  $\text{C}_2\text{H}_4$  selectivity was recorded with increasing temperature. Methyl radicals generated from C–C bond cleavage over h-BN catalysts can undergo four secondary reactions which include oxidative coupling of the methyl groups to produce  $\text{C}_2$  products. The oxidative coupling leads to a better yield of  $\text{C}_2$  products, whilst other processes such as hydrogenation of methyl to form methane and selective oxidation to  $\text{CH}_x\text{O}_y$  serve to lower the  $\text{CO}_x$  selectivity. Although the study did not undertake extensive surface characterisation techniques, the origin of selectivity is explained and may lead to improving conditions and structural properties by mapping the various reaction pathways. For example, isoconversion studies would extend understanding of the reaction mechanism and form a better comparison between h-BN and  $\text{VO}_x/\text{Al}_2\text{O}_3$ .

Advanced characterisation of gas-phase radicals was undertaken by Zhang *et al.*<sup>204</sup> to develop an understanding of reaction pathways of methyl radicals which are formed during C–C bond cleavage. Using synchrotron radiation vacuum ultraviolet photoionization mass spectroscopy (SVUV-PIMS), methyl radicals were detected under reaction conditions (600 °C, ODH- $\text{O}_2$  conditions with BN treated *via* gas exfoliation to increase surface area to  $72.7 \text{ m}^2 \text{ g}^{-1}$ ). The detection of gas phase methyl radicals linked with the kinetic data showed that methyl radicals contribute to  $\text{C}_1$  and  $\text{C}_2$  products. The selective route to propene was expected to be a surface-controlled pathway as no propyl radicals were detected by SVUV-PIMS, despite the group being able to demonstrate a high sensitivity for propyl radicals. Therefore, control of conditions to maximise surface-controlled processes may increase the selectivity to propene and

limit  $\text{C}_1$  and  $\text{C}_2$  products. Both high surface BN and supported oxidised boron catalysts were tested, with both showing formation of gas-phase radicals.

Venegas *et al.*<sup>206</sup> also highlighted the importance of gas-phase reactions in the reaction mechanism over B-based catalysts and suggested that the propyl radicals are not bound to the surface and react with  $\text{HOO}^\bullet$  radicals in the gas-phase. The hypothesis is that if propane reaction pathways were surface-mediated, then similar selectivity-conversion trends to metal oxides would be seen. This is a direct contradiction of the analysis of radicals undertaken using SVUV-PIMS shown previously, which did not detect propyl radicals despite previously showing the capability, and so further elucidation may be needed.

Lu *et al.* investigated various  $\text{B}_2\text{O}_3/\text{SBA-15}$  catalysts. 10 wt% of  $\text{B}_2\text{O}_3$  yielded the highest conversions at 500 °C, while conversion drops above this loading.<sup>207</sup> The supported boron oxide catalysts showed activity at 405 °C, much lower than previous examples of boron-based catalysts. Analysis by  $^{11}\text{B}$  NMR detected four different B environments in fresh and spent catalysts: namely  $\text{B}_3\text{O}_{9/2}$  (boroxol ring),  $\text{BO}_{3/2}$  (non-ring), tri-coordinated planar B species and tetra-coordinated B species. The latter species were fused into the silica matrix. The presence of boroxol ring and non-ring sites was proposed as the reason for activity at lower temperature, but the data presented does not differentiate between the two. Comparison of fresh and spent catalysts showed an increase in the boroxol ring environment and a decrease in  $\text{BO}_{3/2}$ . This suggests a structural change due to oxidative conditions, rather than temperature, as the materials were prepared at 700 °C.<sup>199</sup>

Amorphous  $\text{B}(\text{OH})_x\text{O}_{3-x}$  was identified using  $^{11}\text{B}$  solid state NMR, SEM and XAS after h-BN and BNNTs were exposed to ODH- $\text{O}_2$  conditions. Boron species with different levels of hydroxylation were detected using  $^1\text{H}$ – $^{11}\text{B}$  double resonance experiments<sup>208</sup> to show a wide range of oxidation states associated with boron. A range of oxide bridges, hydroxyl and oxide species were present, which result from oxidation and hydrolysis of BN catalysts. The study clearly demonstrates the complexity of these catalysts under ODH- $\text{O}_2$  conditions, and that *in situ* characterisation of the working catalyst is crucial to understanding the reactivity.

Boron oxide was supported on  $\text{SiO}_2$  to probe how structural control of the surface influences the catalytic performance of boron-containing catalysts. The preparation method employed (calcination of tri-isopropyl borate on an amorphous silica support at 550 °C) formed  $\text{BO}_3$  chains, which cannot be





replenished, unlike h-BN and BNNT. The  $\text{BO}_x/\text{SiO}_2$  material showed a  $\sim 10\%$  lower selectivity for a similar conversion when compared to h-BN, but the loading of B was comparatively low, and the bare  $\text{SiO}_2$  may lower the selectivity.<sup>209</sup> Dual or single boron sites were present with varying levels of oxidation and hydroxylation after exposure to  $\text{ODH-O}_2$  conditions, and the active centre of the catalyst may be one or more of these species. The difficulty in fully understanding the active site in this system is due to the co-existing boron species detected after exposure;  $\text{BO}_3$  and B-OH have both been implicated but conclusive evidence has not been found. The appearance of metaborate and  $\text{BO}_3\text{OH}$  species in the spent catalysts was detected, but there is no data suggesting that these are desirable. It is clear that restructuring of the surface occurs, with a dynamic active site that undertakes  $\text{ODH-O}_2$ . It is also reasonable to expect that a hierarchy of activity exists, where some B species are more active than others, but a multitude of oxidised or hydroxylated boron surface sites can catalyse the reaction. The preparation of single-site boron catalysts would be instructive to understand the active phase.

A h-BN/cordierite monolithic catalyst exhibited a productivity increase of 55% when compared to elemental B. This is among the most active B catalysts reported to date. It was shown that optimising conditions for a high WHSV can lower  $\text{CO}_2$  selectivity to 0%, which is impressive even by the standards of h-BN catalysts.<sup>210</sup> It was hypothesised that the high WHSV did not allow for deep oxidation and therefore limited the formation of  $\text{CO}_x$  products. The monolith surface was characterised using FT-IR to confirm the presence of BN, but the B speciation was not determined. Wang *et al.* speculated that the linear channel structure of cordierite allowed for gas-phase radical chemistry to be enhanced and therefore showed improvement over h-BN powders. The h-BN/cordierite material was prepared by the chemical vapour deposition process. The geometry of the support was essential in this case, as well as the support forming strong oxygen bridge bonds with the catalytic phase.

When comparing macroporous  $\text{BPO}_4$  to bulk  $\text{BPO}_4$ , it was found that the macroporous structure increased the performance significantly. The STY of macroporous  $\text{BPO}_4$  was  $320 \text{ mol}_{\text{C}_3\text{H}_6} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$  (Table 9, entry 6).<sup>211</sup> When using the same WHSV, macroporous  $\text{BPO}_4$  exhibited three-times the conversion of bulk  $\text{BPO}_4$  despite being tested at a  $30^\circ\text{C}$  lower temperature, whilst achieving roughly the same product distribution. The surface area normalised results revealed that both catalysts were equally active, suggesting that the same tri-coordinated B-O species is the active, but an increased number of active sites were formed in the macroporous structure. The interconnected macroporous structure was found to achieve outstanding productivity when exposed to a large WHSV by facilitating efficient mass transfer through the catalyst. As macroporous  $\text{BPO}_4$  and h-BN/cordierite both exhibited a very high STY, it is implied that optimisation of mass transfer *via* engineering porosity has significant impact on the resulting catalyst. These data suggest that the reaction proceeds in the gas-phase, and as long as it can be rapidly

initiated by a large surface area, then a large WHSV will limit surface intermediate contact time, and increase selectivity and turnover frequency.

Overall, it is clear that an important and rapidly developing area of  $\text{ODH-O}_2$  catalysis is the application of boron-based materials. Many reports corroborate that B-O and B-OH species, or a mix between the two (*i.e.*,  $\text{B}(\text{OH}_x)\text{O}_{3-x}$ ) are the active sites for h-BN based catalysts. While many reports examine catalyst design, the specific active site and phase is not well understood. This is to be expected with such a new generation of catalysts, but many papers suggesting different active sites and phases of boron exist, resulting in confusion of how to progress with catalyst improvement. Attempts to understand the mechanism have not yet been validated, and a different range of structures have been concluded to be the active sites. Supported catalysts have been formed and show high productivities and potential advancement in the field, but the fundamental understanding of *in situ* phases and mechanistic processes is still somewhat lacking. It may be beneficial to explore applications of boron-based catalysts in other oxidation reactions and start to build up structure-activity relationships. For example, focussing on bulk and layered materials as well as high surface area materials, may be advantageous in developing an understanding of the intrinsic properties which are desirable when using boron-based catalysts for  $\text{ODH-O}_2$ . Controlling the structure by a consistent synthesis method seems viable, as shown by the formation of nanoporous hexagonal boron nitride nanosheets (h-BNNS) from amorphous h-BN precursors. The h-BNNS catalysts prepared by Chen *et al.*<sup>212</sup> exhibited a surface area of  $347 \text{ m}^2 \text{ g}^{-1}$ , as well as high purity, high crystallinity and increased thermal stability when compared to the amorphous h-BN materials. The dehydrogenation activity was measured using dodecahydro-*N*-ethylcarbazole as the substrate. The h-BNNS catalyst achieved a 34% increase in yield when compared to amorphous h-BN. To build on this, nanoporous h-BNNS could be applied to propane oxidative dehydrogenation, and if this is successful, begin to build structure-activity relationships using these highly crystalline materials.

### 5.3. Other $\text{ODH-O}_2$ catalysts

While the majority of  $\text{ODH-O}_2$  catalysts are based on  $\text{BO}_x$  or  $\text{VO}_x$ , a multitude of other elements have been demonstrated to be active for  $\text{ODH-O}_2$ . In this section the most significant reports are critically reviewed and compared to the state-of-the-art  $\text{VO}_x$ - and  $\text{BO}_x$ -based  $\text{ODH-O}_2$  catalysts. Cavani *et al.* compiled an extensive literature review in 2007, where  $\text{MoO}_x$ -based catalysts were shown to have a lower catalyst performance when compared to analogous vanadia based catalysts for the  $\text{ODH-O}_2$  reaction.<sup>213</sup> A direct comparison of kinetic parameters for  $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$  and  $\text{MoO}_3/\text{Al}_2\text{O}_3$  in the  $\text{ODH-O}_2$  reaction showed that vanadia-based catalysts had higher selectivity at isoconversion, and were more reducible than the analogous  $\text{MoO}_x$ -based catalysts.<sup>214</sup> The V and Mo catalysed  $\text{ODH-O}_2$  reaction proceed *via* similar mechanisms. When comparing V-based catalysts to Mo-based catalysts, both supported on



ZrO<sub>2</sub>, it was found that Mo was less active as the catalyst showed a higher activation energy.<sup>215</sup>

Mo=O bonds were found to be active for C-H abstraction, with the strength of the Mo=O bond influencing the activity: the stronger the bond, the lower the activity. Furthermore the strength of the Mo=O bond was shown to be influenced by MoO<sub>x</sub> loading. The bridging oxygen bond between Mo and the support was found to be active in the complete combustion of propane.<sup>216</sup> The reactivity of Mo–O–M anchoring bonds is influenced by the cation electronegativity in the support material; a low support cation electronegativity leads to increased basicity of the bridging oxygen, and therefore has a higher activity for redox processes.<sup>217</sup> Analysing speciation of MoO<sub>x</sub> on ZrO<sub>2</sub> supports found that two dimensional polymolybdate species dominated the surface up to loadings of 5 Mo atoms nm<sup>−2</sup> and that further increasing Mo concentration led to a lower activity per Mo atom, ascribed to either limiting access to active sites or strengthening of the Mo=O bond.<sup>216</sup>

The selectivity of MoO<sub>x</sub>/ZrO<sub>2</sub> can be increased by the addition of alkali metal dopants to reduce Lewis acidity of the Mo<sup>6+</sup> centres allowing propene to desorb more effectively, thus decreasing the rate of consecutive oxidation reactions.<sup>218</sup> However, the overall performance of the catalyst was lower due to decreased reducibility, which inhibited the Mo<sup>6+</sup> centre from undertaking C–H abstraction. A typical conversion selectivity trend was seen, where selectivity decreases with an increase in conversion. When MoO<sub>x</sub> was supported on Al<sub>2</sub>O<sub>3</sub>, MoO<sub>3</sub> crystallites formed above 4.5 Mo atoms nm<sup>−2</sup>. Below a surface density of 4.5 Mo atoms nm<sup>−2</sup>, the polymolybdate regions were abundant and ODH-O<sub>2</sub> rates were high. Above monolayer surface coverage (4.5 Mo atoms nm<sup>−2</sup>), the formation of MoO<sub>3</sub> crystallites occurred which limited the number of exposed Mo–O sites. Unlike VO<sub>x</sub> catalysts where V<sub>2</sub>O<sub>5</sub> crystallites reduce selectivity, the presence of MoO<sub>3</sub> crystallites were not detrimental to selectivity, just the intrinsic activity. Bridging oxygen bonds between the support and Mo for both Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> were found to be active for propane combustion to CO<sub>x</sub>, in a similar manner to VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts.

The above studies of Mo-based catalysts have shown that they are limited when compared to analogous V-based catalysts. A selectivity increase is found for increasing molybdenum loadings up to 10 wt%, indeed suggesting that polymeric MoO<sub>x</sub> up to monolayer coverage gives the best selectivity. However, selectivity was slightly lower at the same conversion when compared to 2 wt% V catalysts.<sup>219</sup> Reports involving Mo containing catalysts often concern mixed metal oxide catalysts containing both V and Mo. When comparing Mo-only to mixed Mo and V oxide catalysts formed *via* flame spray pyrolysis, a Mo-only loading of 10 wt% on Al<sub>2</sub>O<sub>3</sub> (10Mo/Al<sub>2</sub>O<sub>3</sub>) gave a yield of 9.4%, compared to a mixed catalyst containing 4 wt% Mo and 2 wt% V (4Mo2V/Al<sub>2</sub>O<sub>3</sub>) reaching a yield of 10% (Table 10, entries 8 and 10). The relative rate of oxidation of propene to CO<sub>x</sub> products, when compared to oxidative dehydrogenation of propane, was found to be lower for 4Mo2 V/Al<sub>2</sub>O<sub>3</sub> than 10Mo/Al<sub>2</sub>O<sub>3</sub> between 350–500 °C. A Mo/V ratio of 2 gave the highest yield for the mixed Mo/V catalysts, and the synergistic nature of the two metals leads to the suppression of overoxidation. This research was limited in that it did not contain any *in situ* characterisation to probe the synergistic nature of the metal species. Interestingly, V catalysts formed *via* co-impregnation with Mo exhibited a V–O binding energy increase which limited overoxidation as the oxygen became less labile.<sup>220</sup> Mo also increased the concentrations of V<sup>4+</sup> and V<sup>3+</sup> species, which are more selective than V<sup>5+</sup> entities. The strength of the V–O bond can therefore be carefully controlled by level of Mo doping, which may be the origin of synergistic properties which were observed for 4Mo2 V/Al<sub>2</sub>O<sub>3</sub> catalysts.

The cycling of Mo-only catalysts has also been explored.<sup>221</sup> Interestingly, propene selectivity increased by 15% for the second ODH-O<sub>2</sub> phase, at a similar propene conversion, leading to an overall propene yield increase of 5%. *In situ* XANES showed that the oxidation state of Mo in the second ODH-O<sub>2</sub> phase was between +6 and +4 (corresponding tetrahedral and octahedral coordination respectively), with the change from the initial +6 environment happening under the DDH conditions. The distorted structure between +6 and +4

**Table 10** Catalytic performance in ODH-O<sub>2</sub> for catalysts which are not vanadia or boron-based

Entry	Catalyst	T/°C	O <sub>2</sub> /C <sub>3</sub> H <sub>8</sub>	WHSV/h <sup>−1</sup>	X <sub>C<sub>3</sub>H<sub>8</sub></sub> /%	S <sub>C<sub>3</sub>H<sub>6</sub></sub> /%	STY/mol <sub>C<sub>3</sub>H<sub>6</sub></sub> kg <sub>cat</sub> <sup>−1</sup> h <sup>−1</sup>	Ref.
1	Co <sub>3</sub> O <sub>4</sub> /ZIF-8	250	1	11.8	7.1	40.8	7.2	232
2	NiCeO <sub>x</sub>	375	1	3.0	30.3	39.4	7.4	230
3	NiO-polyoxometalate	450	4	0.47	44	45	2.0	227
4	5CrO <sub>x</sub> –MgO	450	0.5	5.9	10.8	84.1	11	234
5	NiO–SPP	450	1	11.8	21	50	26	228
6	B–NiMoO <sub>4</sub>	475	1.25	3.2	18.2	63.8	8.4	243
7	Mesoporous NiMoO <sub>4</sub>	500	2	2.4	11.8	60.1	3.5	225
8	10Mo/Al <sub>2</sub> O <sub>3</sub>	500	5	3.9	32.0	29.4	7.8	219
9	NiO–CeO <sub>2</sub>	500	1	10.0	52	72	79	229
10	4Mo2V/Al <sub>2</sub> O <sub>3</sub>	500	5	15.6	34.0	29.4	33	219
11	g-C <sub>3</sub> N <sub>4</sub>	515	0.25	1.4	23.9	58.5	4.0	238
12	0.5Pt–5Sn/Si-beta	550	0.5	4.7	48	79	40	241
13	NiMoO <sub>4</sub> with Ni/Mo ratio 0.4	600	1	2.4	32.5	48	7.7	223

T = reaction temperature; O<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> = molar ratio of O<sub>2</sub>:C<sub>3</sub>H<sub>8</sub> in the reaction, X<sub>C<sub>3</sub>H<sub>8</sub></sub> = initial propane conversion, S<sub>C<sub>3</sub>H<sub>6</sub></sub> = initial propene selectivity, STY = space time yield. The value next to element/phase represents wt% loading.



oxidation state of Mo is seemingly more selective than the tetrahedral Mo moieties in the original catalyst. *In situ* characterisation has thus highlighted a key structure–property relationship which will be useful in guiding future ODH-O<sub>2</sub> catalysts based on Mo.

Mo supported on titanate nanotubes (Mo-TNT) is a rare example of a supported Mo catalyst being developed in recent years. Mo-TNT was explored due to MoO<sub>x</sub>/TiO<sub>2</sub> showing high dispersion,<sup>217</sup> an effect that was limited by anatase titania having a low surface area. Doping with K, according to a Mo/K ratio of 10, led to increased dispersion of MoO<sub>x</sub> across the TNT surface, achieving a conversion of 21.2% and selectivity of 53.3%.<sup>222</sup> The increased dispersion caused by doping the titanate with K led to an increase in propene yield by 20% when compared to undoped Mo-TNT catalysts, despite a lower conversion.

Transition metal binary molybdates have also been investigated for ODH-O<sub>2</sub> activity. For instance, nickel molybdate catalysts have been shown to be active for ODH-O<sub>2</sub>.<sup>223</sup> Increased selectivity was found to be directly correlated with an increase in Mo/Ni ratio. Further investigation of phases present found that NiO, whilst showing complete conversion, favoured over-oxidation, whereas  $\alpha$ -NiMoO<sub>4</sub> was more active for propane conversion, and  $\beta$ -NiMoO<sub>4</sub> was more selective. A Mo/Ni ratio of 0.4 gave the highest propane yield of 15.6% (Table 10, entry 13), which was ascribed to the high ratio of  $\beta$ -NiMoO<sub>4</sub>/ $\alpha$ -NiMoO<sub>4</sub>, the mesoporous structure and redox properties. Although the activity was identified as being sensitive to the phases present, the underlying properties of each phase were not individually explored.

Chen *et al.* reported that nickel molybdates were active for ODH-O<sub>2</sub> and in particular the  $\alpha$ -NiMoO<sub>4</sub> phase exhibited an enhanced yield compared to NiO and  $\beta$ -NiMoO<sub>4</sub>.<sup>224</sup> Physical grinding of Mo and Ni precursors also led to the absence of NiO in  $\alpha$ -NiMoO<sub>4</sub> when compared to the analogous co-precipitation technique. It was shown that NiMoO<sub>4</sub> had enhanced ODH-O<sub>2</sub> performance when comparing mesoporous to bulk catalysts, but only due to the enhanced number of active sites related to the increased surface area, and not the improved mass transfer properties that usually accompany mesoporosity.<sup>225</sup> The mesoporous catalysts had a lower specific productivity due to the loss of MoO<sub>3</sub> from the surface of the catalysts during synthesis. This confirmed that MoO<sub>3</sub> exhibits favourable activity to NiMoO<sub>4</sub> for the ODH-O<sub>2</sub> reaction (Table 10, entry 7).

NiO has been found to be detrimental to ODH-O<sub>2</sub> selectivity, favouring overoxidation products. Nb was found to be a superior dopant for NiO based catalysts, due to a reduction in the surface concentration of electrophilic O species and increased surface acidity. However, propene was still not the major product over NiO at around 10% conversion,<sup>226</sup> suggesting that NiO-based catalysts are limited in their application for ODH-O<sub>2</sub>. In comparison to Nb-NiO catalysts,  $\alpha$ -NiMoO<sub>4</sub> showed a selectivity of ~75% at roughly 10% conversion, with propene being the major product at similar conversions to Nb-NiO. The NiO-polyoxometalates have been shown

to stabilise the adsorbed oxygen at the surface, which would limit overoxidation,<sup>227</sup> leading to the conclusion that NiO oxygen is too labile to achieve a high selectivity. When undertaking surface polymeric phosphate modification of NiO nanoparticles (NiO-SPP), an increase in selectivity of 2–3 times for NiO-SPP's at isoconversion was shown (Table 10, entry 5).<sup>228</sup> This is due to the polymeric phosphates weaker interaction with propene when compared to NiO nanoparticles, leading to a higher desorption rate and therefore higher selectivity.

CeO<sub>2</sub> was found to be a selective catalyst when HCl was added to the gas feed with O<sub>2</sub>.<sup>229</sup> O<sub>2</sub> was hypothesised to have filled the oxygen vacancies at the surface, forming O<sub>2</sub><sup>2-</sup> species, which mediated the oxidation of Cl<sup>-</sup> to Cl radicals and resulted in high conversion and selectivity to propene. Once again, radical driven routes showed a high selectivity of 72% and conversion of 52% when the CeO<sub>2</sub> was combined with 8 wt% NiO as NiO was shown to enhance the Cl surface coverage which in turn enhanced the route to selective conversion of propane (Table 10, entry 9). Ni was confirmed to increase oxygen vacancies when incorporated into the CeO<sub>2</sub> lattice, leading to an increase in active sites.<sup>230</sup> XPS studies showed O vacancies doubled in concentration over 250 min, causing the selectivity to drop to 25.2%. Whilst oxygen vacancies are necessary to activate oxygen, they decreased selectivity in the absence of HCl,<sup>231</sup> which is why CeO<sub>2</sub> was shown to have a much lower selectivity without the presence of HCl; a change of active species from oxygen vacancies to Cl radical like species, has been shown to increase selectivity without a large detrimental effect on conversion. However, the space time yields observed are significantly lower than the most active ODH-O<sub>2</sub> catalysts.

Co-Based catalysts have been investigated for ODH-O<sub>2</sub>, but their performance is also limited and vastly inferior to V- or B-based catalysts. However, Wang *et al.* developed a Co<sub>3</sub>O<sub>4</sub>/ZIF-8 catalyst that could operate at 250 °C, which is about 200 °C lower than the operating temperature for many ODH-O<sub>2</sub> catalysts.<sup>232</sup> Such low temperature activity warrants further investigation, but the reported space time yield of 7.2 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> (Table 10, entry 1) is relatively low for an ODH-O<sub>2</sub> catalyst. Tanasoi *et al.* investigated various mixed metal oxides derived from layered double hydroxide precursors. CoMgAlO<sub>x</sub> exhibited the highest propene yield, but the propene selectivity was limited due to an increase in cracking, which then led to overoxidation.<sup>233</sup> There was no correlation between reducibility and catalyst performance, suggesting that redox properties are not rate-determining in these ODH-O<sub>2</sub> catalysts. Unfortunately, the balance of acid and base sites was not measured, so a possible correlation in this respect was not identified.

Although CrO<sub>x</sub>-based catalysts have been widely investigated for DDH and ODH-CO<sub>2</sub>, there is limited research available for CrO<sub>x</sub>-catalysts for ODH-O<sub>2</sub>. Some CrO<sub>x</sub>-type catalysts have been shown to form propene, with the selective phase being Cr<sub>5</sub>O<sub>12</sub> when supported on nano-crystalline MgO.<sup>234</sup> The space time yield was calculated to be 11.3 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> (Table 10, entry 4), which is significantly less than Cr catalysts



for DDH and about equivalent to the performance of  $\text{CrO}_x$  catalysts for ODH- $\text{CO}_2$ . When supported on carbon nanotubes, the presence of  $\text{Cr}_2\text{O}_3$  increased the  $\text{C}=\text{O}$  active sites on the carbon nanotubes, whilst also increasing propene desorption,<sup>235</sup> suggesting that Cr promotes the functionality of the carbon active centre.

Nanocarbons are an emerging field of catalysts for alkane dehydrogenation. Frank *et al.* showed that propane can be activated by surface oxygen groups on oxidised carbon nanotubes, noting that  $\text{sp}^2$  hybridised carbon species are selective and stable for ODH- $\text{O}_2$ , and that carbon nanotubes provide a balance between reactivity ( $\text{sp}^3$ ) and stability ( $\text{sp}^2$ ).<sup>236</sup> Nanocarbons also show high selectivity to alkenes when compared to metal oxides, but the intrinsic activity is lower. And additional feature of nanocarbons is that they are tuneable; N or B doping within the lattice leads to a change in electronic structure which can influence intrinsic catalytic activity, whilst changing surface functionality can influence selectivity. For example, adding  $\text{B}_2\text{O}_3$  to the surface inhibits the activity of electrophilic oxygen species which promote overoxidation. Interestingly, this is one of the first examples of using  $\text{B}_2\text{O}_3$  for ODH- $\text{O}_2$ , where it acts to inhibit the activity through functionalisation of the surface, leading to an increased selectivity. More recently, Qi *et al.* confirmed the ketonic carbonyl groups to be the active site for general ODH reactions, whilst also confirming the effects of  $\text{B}_2\text{O}_3$ .<sup>237</sup> The unique chemical structure of nanocarbons means that the reaction mechanism does not operate under a Mars-van Krevelen or Langmuir-Hinshelwood route. *In situ* characterisation and measurements proved vital to finding the reaction mechanism for nanocarbons; *in situ* experiments for the oxidative dehydrogenation of ethylbenzene using nanocarbons showed the redox cycle of carbonyl-hydroxyl groups being the basis for the reaction mechanism.

Recently, Cao *et al.* discovered that graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ) are highly selective to propene (75%) at a moderate conversion of 12.8%. Additionally, selectivity to ethene was 15%, meaning total olefin selectivity was around 90%. The highest STY was measured at 515 °C to be  $4.0 \text{ mol}_{\text{C}_3\text{H}_6} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$  (Table 10, entry 11).  $\text{g-C}_3\text{N}_4$  is analogous to graphite in structure, as is h-BN. The rate dependence of propane was first order, which is different to h-BN, but it was found to be the same as h-BN regarding the rate dependence of oxygen. DFT calculations suggested this first-order rate dependence of propane was due to simultaneous H abstraction by carbonyl species, which are similarly distant from one another when compared with the distance between the C-H bonds in propane. The simultaneous H abstraction would therefore lead to a lower concentration of the  $\text{C}_3\text{H}_7^*$  reaction intermediate, as well as an increased  $\text{O}_2/\text{O}^*$  ratio and therefore a lower likelihood of overoxidation.<sup>238</sup> This new route to propene shows promise and enhances our understanding of selectivity patterns. The materials were shown to be activated in a similar way to h-BN, forming the proposed active site, *i.e.*, carbonyl bonds, on the surface under oxidative conditions. Under these oxidative conditions, the surface area increased from  $8.9 \text{ m}^2 \text{ g}^{-1}$  to  $78.1 \text{ m}^2 \text{ g}^{-1}$ , due to the formation of mesopores at the surface. The large

increase in surface area when compared to the starting material, was a large factor in obtaining the high activity.

While supported precious metal clusters are amongst the most researched class of catalyst for DDH (and are used in some industrial processes) their application in ODH- $\text{O}_2$  has been relatively limited. Preliminary research into supported Pt metal clusters for ODH- $\text{O}_2$  was reported in the early 90s, with studies comparing particle-support interactions and the influence of supports on the reaction. Notably, Hubbard *et al.* reported Pt/ $\text{ZrO}_2$  showed at least one order of magnitude higher activity than Pt/ $\gamma\text{-Al}_2\text{O}_3$ .<sup>239</sup> This is due to  $\gamma$ -alumina seemingly deactivating the Pt, which was confirmed due to the small Pt particles on  $\gamma$ -alumina having a higher reduction temperature when compared to bulk Pt.

To achieve high activity in supported metal catalysts, the dispersion of the supported metal must be optimised in order to maximise the number active centres and allow efficient use of the precious metal itself, which is often the most expensive component of the catalyst. Additionally, particle size and activity may not scale linearly. Vajda *et al.* reported that supported under-coordinated  $\text{Pt}_{8-10}$  clusters were highly active for ODH- $\text{O}_2$ .<sup>240</sup> The activity of the catalyst in this study was shown to be much larger than the more commonly used vanadia-based catalysts, whilst showing a higher selectivity. The key to an increased activity was due to the under-coordinated Pt cluster strongly adsorbing the propane when compared to an extended Pt surface, confirmed by catalytic data which was in agreement with DFT. DFT showed a significant weakening of the C-H bond when propane interacts with under-coordinated Pt clusters in comparison to Pt(111) surface.

Combining Pt clusters with Sn showed increased productivity due to the electron transfer between the Pt and Sn which were in close proximity. 0.5Pt-5Sn/Si-beta exhibited a STY of  $40 \text{ mol}_{\text{C}_3\text{H}_6} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$  (Table 10, entry 12).<sup>241</sup> Pt-Sn catalysts were characterised *via*  $\text{C}_3\text{H}_8$ -TPD and  $\text{C}_3\text{H}_6$ -TPD. In comparison to 0.5Pt/Si-Beta and 5Sn/Si-beta, 0.5Pt-5Sn/Si-beta showed that the combination of the Pt and Sn led to a stronger adsorption of propane to allow for increased activity and propene desorbed more readily, leading to the understanding that propene would not be further oxidised to  $\text{CO}_x$  products due to a higher rate of desorption. It was also found that Pt-Sn/SAPO-34 catalysts showed an increased conversion when oxygen was introduced into the gas feed (compared to DDH conditions).<sup>242</sup> This was due to the oxygen reacting with hydrogen to form water and driving the equilibrium towards propene formation. Conversion largely depended on the  $\text{C}_3\text{H}_8:\text{O}_2$  ratio: an increase in propane conversion was found with an increase in  $\text{O}_2$  concentration relative to propane concentration, but too high an oxygen concentration caused overoxidation to  $\text{CO}_x$ . The activity and selectivity were much higher for Pt-Sn/SAPO-34 – a yield of 72.4% as compared to a ~10–15% yield for most V based catalysts. Introducing oxygen into the feed also reduced the formation of coke, which is a feature of instability in DDH. Water formed *via* ODH- $\text{O}_2$  was found to reduce stability, by increasing sintering of Pt due to a weaker metal-support interaction.<sup>242</sup> Pt-Sn catalysts are of





course widely studied for DDH and are found in industrial catalysts, as described above.

In summary, a variety of different catalysts have been shown to be active and selective for ODH-O<sub>2</sub>. While vanadia- and boron-based catalysts comprise a large proportion of the reports to date, Ni-based catalysts have shown promise, particularly NiO-CeO<sub>2</sub>. Mo-Based catalysts also prominently feature but are currently limited in comparison to analogous metal oxide catalysts, with low propene selectivity at moderate propane conversion. Graphitic carbon nitride, g-C<sub>3</sub>N<sub>4</sub>, although much less active than NiO<sub>x</sub> per kg, exhibited high selectivity to olefins at moderate propane conversion and may warrant further investigation to maximise performance. High surface area, porous C<sub>3</sub>N<sub>4</sub> may be a strong candidate to produce an active and selective catalyst.

ODH-O<sub>2</sub> offers many inherent advantages as the reaction is exothermic, thermodynamically unlimited and avoids formation of coke. Overall, extensive research into VO<sub>x</sub>-based catalysts has been undertaken, with the clear limitation being overoxidation to CO<sub>x</sub> products, but recent developments with one-step preparations and grafting techniques have improved catalyst performance to be comparable with the most active DDH Pt- and CrO<sub>x</sub> catalysts. Deep oxidation remains a challenge for VO<sub>x</sub> and other supported metal oxides. However, it is clear that B-based catalysts, although recently developed and less understood in both structure and mechanism, have clear potential for commercialisation due to the high selectivity at high propane conversion. Additionally, ethene is formed as a secondary product. Many B-based catalysts have similar, if not higher, STYs compared to DDH catalysts. Furthering the understanding of the reaction mechanism is essential to developing more efficient catalysts, and this appears to be the focus of recent research in the literature.

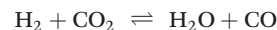
## 6. Oxidative dehydrogenation with carbon dioxide

The so-called 'soft-oxidation' of propane using CO<sub>2</sub> was proposed as an alternative process to using O<sub>2</sub> in order to decrease overoxidation to products such as CO and CO<sub>2</sub>. In the context of the global effort to reduce anthropogenic CO<sub>2</sub> emissions, the ODH-CO<sub>2</sub> reaction has gained a renewed interest. CO<sub>2</sub> utilisation technologies are of general interest to develop a circular economy, but it is important to acknowledge that the current demand for propene (*ca.* 130 million tonnes per annum<sup>1</sup>) is a small fraction of the annual CO<sub>2</sub> emissions from fossil fuels (35 Gt).<sup>244</sup> Therefore the ODH-CO<sub>2</sub> process is unlikely to make a significant impact on global emissions. Additionally, there is an increased cost associated with obtaining concentrated CO<sub>2</sub> compared to using air, as could be envisaged in an ODH-O<sub>2</sub> process. It could be argued that commercial ODH-CO<sub>2</sub> processes would significantly reduce the carbon footprint of an individual chemical or industrial plant that would otherwise release CO<sub>2</sub> into the atmosphere, but this would depend on how CO is used as a by-product in the reac-

tion. CO<sub>2</sub> was initially utilised in the dehydrogenation of ethylbenzene,<sup>245</sup> but since then has been reported for other alkane substrates, including ethane and butane.<sup>246</sup> The addition of CO<sub>2</sub> in the dehydrogenation reaction has multiple effects: As discussed in Section 2, it facilitates the RWGS reaction which removes H<sub>2</sub> from the system and shifts the thermodynamic equilibrium limit to favour propene production. Additionally, CO<sub>2</sub> can dissociate on the surface of a catalyst and provide O species to dehydrogenate propane directly. Finally, it can react with coke *via* the reverse-Boudouard reaction to produce CO, which can potentially extend the lifetime of the catalyst.

As an acidic molecule, carbon dioxide will preferentially adsorb on basic sites, which is in contrast to propane which will adsorb on acidic sites. Therefore, the correct balance of acidic and basic sites is a key consideration in catalyst design. Equally, the ratio of carbon dioxide to propane is important to take in account, as it has kinetic and thermodynamic implications. Thermodynamically, higher CO<sub>2</sub>:C<sub>3</sub>H<sub>8</sub> ratios limit coke forming side-reactions.<sup>22</sup> Interestingly, the addition of carbon dioxide has been found in some cases to be detrimental to the catalyst performance;<sup>247</sup> this underlines the dependency of catalytic reactivity on the structure of the catalyst.

Generally, there are two proposed reaction pathways that describe the soft oxidation of propane to propene. These are described as the direct and indirect pathways:



In the direct pathway, oxygen from CO<sub>2</sub> abstracts the H from propane, forming H<sub>2</sub>O as a primary product. Conversely, in the indirect pathway the dehydrogenation occurs in the absence of an oxidant, and the role of CO<sub>2</sub> is to remove H<sub>2</sub> *via* the RWGS reaction. It should be noted that regardless of the pathway, the RWGS reaction must mediate the balance of H<sub>2</sub>O, CO, CO<sub>2</sub> and H<sub>2</sub>, although the contribution of RWGS to the final product distribution is often overlooked. In the following sub-sections, the literature reports concerning catalysts for ODH-CO<sub>2</sub> are reviewed and discussed.

### 6.1. Chromium-based ODH-CO<sub>2</sub> catalysts

Chromium oxide is one of the most widely investigated catalysts for the DDH reaction and as described above, is a key component of the industrial CATOFIN process. It is also one of the earliest reported transition metal oxide catalysts for the soft oxidation of propane to propene. Generally, the studies of Cr<sub>2</sub>O<sub>3</sub>-catalysed ODH-CO<sub>2</sub> reactions are carried out under similar conditions to the DDH process, but with the addition of CO<sub>2</sub> to the gas-feed, typically supplied as a 1:1 ratio or in excess of the partial pressure of propane. The performance and reaction conditions of some reported catalysts are shown below in Table 11.

The first study of Cr<sub>2</sub>O<sub>3</sub>-based catalysts for ODH-CO<sub>2</sub> was reported by Takahara *et al.* in 1996 using Cr<sub>2</sub>O<sub>3</sub> supported on SiO<sub>2</sub>, activated carbon (AC) or Al<sub>2</sub>O<sub>3</sub>. The catalyst tests were



**Table 11** Comparison of the catalytic performance of selected Cr-based catalysts for ODH-CO<sub>2</sub>

Entry	Catalyst	T/°C	CO <sub>2</sub> /C <sub>3</sub> H <sub>8</sub>	WHSV/g <sub>C<sub>3</sub>H<sub>8</sub></sub> g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	X <sub>C<sub>3</sub>H<sub>8</sub></sub> /%	S <sub>C<sub>3</sub>H<sub>6</sub></sub> /%	STY/mol <sub>C<sub>3</sub>H<sub>6</sub></sub> kg <sup>-1</sup> cat h <sup>-1</sup>	Ref.
1	RuCrO <sub>x</sub> /SiO <sub>2</sub>	496	1	7.9	9	85	13	266
2	5%Cr <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	500	2	—	15	83	—	267
3	Cr <sub>2</sub> O <sub>3</sub> -(15 wt%)Al <sub>2</sub> O <sub>3</sub>	550	1	—	4.7	91.3	—	248
4	10%Cr <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	550	2	0.30	51.1	81.7	2.6	251
5	CrO <sub>x</sub> /Na-ZSM-5	550	2	0.30	48	86	2.5	261
6	CrO <sub>x</sub> -mesoporous ZrO <sub>2</sub>	550	2	0.30	68	60	2.5	252
7	CrO <sub>x</sub> /SBA-15	550	2	0.30	24.2	83.9	1.9	250
8	CrO <sub>x</sub> /ZrO <sub>2</sub>	550	2.6	0.3	40	88	2.2	253
9	5%CrO <sub>x</sub> /AC	550	5	3.0	39.8	86.7	21	260
10	CrO <sub>x</sub> /MCM-41	550	5	1.2	40	90	8.9	88
11	Cr <sub>2</sub> O <sub>3</sub> /beta-zeolite	550	5	1.2	33	81.6	6.6	263
12	7% CrO <sub>x</sub> /SBA-1	550	5	1.2	37.7	85.8	7.9	85
13	3.4% Cr <sub>2</sub> O <sub>3</sub> /SBA-1	550	5	1.2	33.2	87.9	7.2	84
14	0.5Ni-CrO <sub>x</sub> /SBA-15	600	1	1.8	25	90	8.3	264
15	CrO <sub>x</sub> /B-MFI	600	1	1.1	22.1	91	4.7	262
16	CrO <sub>x</sub> /SiO <sub>2</sub>	600	4	1.2	70	79	14	258
17	CrO <sub>x</sub> /SiO <sub>2</sub>	600	5	1.2	41	65	6.6	256
18	CrO <sub>x</sub> /SiO <sub>2</sub>	600	7	0.89	36.3	92	6.2	254
19	CrO <sub>x</sub> /SiO <sub>2</sub>	600	1	1.8	40	90	13	259
20	CrO <sub>x</sub> /SBA-1	600	5	1.2	39.4	86.6	8.4	257

T = reaction temperature; CO<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> = molar ratio of CO<sub>2</sub>: C<sub>3</sub>H<sub>8</sub> in the reaction, X<sub>C<sub>3</sub>H<sub>8</sub></sub> = initial propane conversion, S<sub>C<sub>3</sub>H<sub>6</sub></sub> = initial propene selectivity, STY = space time yield. AC = activated carbon.

performed at 600 °C with a feed of propane and argon or carbon dioxide.<sup>248</sup> It was found that over 5 wt% Cr<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>, the propene yield increased from 6.5% to 9.1% when CO<sub>2</sub> was co-fed instead of Ar. In contrast, the alumina supported catalyst was inhibited by the addition of CO<sub>2</sub>, as shown by the drop in propene yield from 12.7% to 3.3%. The 5 wt% Cr<sub>2</sub>O<sub>3</sub>/AC material was unaffected by CO<sub>2</sub> addition. The Cr<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> catalyst deactivated rapidly, retaining just 66% of its original activity after 4 h on-stream. The stability was noted to be the same with or without CO<sub>2</sub> in the reactant feed. Not only did this study establish Cr<sub>2</sub>O<sub>3</sub> as an active ODH-CO<sub>2</sub> catalyst, it also captured one of the recurring themes in catalyst design for ODH-CO<sub>2</sub>: some catalysts are inhibited by the addition of CO<sub>2</sub> while others perform much better.

Relative to many other metal oxides, Cr<sub>2</sub>O<sub>3</sub> is considered to be one of the most promising catalysts for ODH-CO<sub>2</sub>. Takehira *et al.* compared the catalytic performance of several d block and p block oxides (namely Cr, Ga, Ni, V, Fe, Mn and Co) supported on MCM-41, at 550 °C with a CO<sub>2</sub>: C<sub>3</sub>H<sub>8</sub> molar ratio of 5.6.<sup>91</sup> After 30 min on-stream, the propene yield of the Cr-based catalyst was 15% whereas for the Ga-based counterpart it was 5%. The remaining catalysts all exhibited lower propene yields (in the 1–4% range). However, as the catalysts were not characterised, it is unclear if the dispersion of these catalysts was comparable, and therefore if the results reflect the true intrinsic activity of each metal. It was also noted that the order of reactivity resembled the trends observed by Nakagawa *et al.* for diamond-supported metal catalysts in the DDH reaction.<sup>249</sup> This suggests that there are commonalities in catalyst design between DDH and ODH-CO<sub>2</sub> which most likely relate to the interaction of the alkane with the catalyst.

Contrary to this, Zhang *et al.* compared ZrO<sub>2</sub>, SBA-15 and γ-Al<sub>2</sub>O<sub>3</sub> as supports for Cr<sub>2</sub>O<sub>3</sub> in the DDH, ODH-CO<sub>2</sub> and

ODH-O<sub>2</sub> reactions.<sup>250</sup> They found that the highest propene yield was observed with different catalyst systems under different dehydrogenation reactions, *i.e.*, the activity trends in DDH did not translate to ODH-CO<sub>2</sub> catalysts. Specifically, Cr<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalyst was the most active for the DDH reaction, while the highest yield of propene for the ODH-CO<sub>2</sub> and ODH-O<sub>2</sub> reactions was observed over Cr<sub>2</sub>O<sub>3</sub>/SBA-15 (Table 11, entry 7). Across all the catalysts however, the highest propene yields were generally observed in the DDH reaction, ascribed to the production of carbon oxides in the ODH-O<sub>2</sub> and ODH-CO<sub>2</sub> reactions. However, it was reported that Cr<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> was more stable on-stream in ODH-CO<sub>2</sub> than in the DDH reaction. Wu *et al.* also observed increased stability of Cr<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> in the presence of CO<sub>2</sub> (Table 11, entry 4).<sup>251</sup> They reported that the CO formation rate was higher than the CO<sub>2</sub> consumption rate and the excess CO was suggested to originate from the Boudouard reaction (CO<sub>2</sub> + C → 2CO); this could explain the increased stability of this catalyst. It is possible that some dry reforming of propane also took place, which would produce H<sub>2</sub> and CO. Zhao *et al.* recently reported the facile preparation of Cr supported in mesoporous ZrO<sub>2</sub> using an evaporation-induced self-assembly method (Table 11, entry 6).<sup>252</sup> The authors suggested that propene could react with carbon dioxide to form carbon monoxide, methane and water. Other studies have reported a stronger inhibition effect for Cr<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalysts in the presence of CO<sub>2</sub>. For instance, Ferreira *et al.* studied the adsorption properties of CO<sub>2</sub> and concluded that it binds strongly to active Cr<sub>2</sub>O<sub>3</sub> sites, lowering the activity and stability of the catalyst,<sup>253</sup> whereas Xie *et al.* suggested that coke formation could originate from CO<sub>2</sub> hydrogenation over Cr<sup>2+</sup> species. These conflicting reports may relate to the structural polymorph of ZrO<sub>2</sub> present in the catalyst support; this factor is often overlooked, but recent studies



from Kondratenko *et al.* revealed that nanocrystalline  $\text{ZrO}_2$  is an active DDH catalyst in its own right<sup>151,152</sup> under similar reaction conditions. The  $\text{ZrO}_2$  crystal phase and crystallite size were strongly correlated to the catalyst activity: smaller crystallites were more active but amorphous  $\text{ZrO}_2$  had very low intrinsic activity. Moreover, monoclinic  $\text{ZrO}_2$  was more active than tetragonal  $\text{ZrO}_2$ .

$\text{Cr}_2\text{O}_3$ -catalysed ODH- $\text{CO}_2$  has been examined over different polymorphs of  $\text{SiO}_2$ ,<sup>254–256</sup> including various structured porous oxides, including SBA-1,<sup>84</sup> SBA-15,<sup>250,257</sup> MCM-41,<sup>91</sup> amorphous silica<sup>84</sup> and mesoporous silica spheres.<sup>258</sup> Notably, Michorczyk *et al.* reported a detailed comparison of different silica supports, coupled with an in-depth characterisation study.<sup>84</sup> It was shown that in each case, the same active Cr species was formed, namely  $\text{Cr}^{6+}$ , but higher surface area silicas (e.g., SBA-1 and SBA-15) were able to facilitate a higher number of such sites. A clear correlation was found between the rate of propene formation and the wt% of  $\text{Cr}^{6+}$ , as determined using X-ray photoelectron spectroscopy (XPS). In DDH, while  $\text{Cr}^{6+}$  is considered active, under reaction conditions  $\text{Cr}^{3+}$  is rapidly formed and considered the principle active species.<sup>93,94</sup> The selectivity to propene was similar across the different silica supports (88–93%), with the observed differences being attributable to differences in propane conversion rather than catalytic properties. These  $\text{Cr}_2\text{O}_3/\text{SiO}_2$  catalysts were highly active at 550 °C and the most active catalyst ( $\text{Cr}_2\text{O}_3/\text{SBA-1}$ ) achieved a STY of  $7.9 \text{ mol}_{\text{C}_3\text{H}_6} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$ , as shown in Table 11, entry 12. It should be noted that the experiments were carried out with a  $\text{CO}_2:\text{C}_3\text{H}_8$  ratio of 5, which as discussed above, has been shown to enable a higher equilibrium yield of propene. Therefore, in studies where high conversions are generally targeted and carbon dioxide is in excess of propane, higher propene yields are reported.

Takehira *et al.* carried out X-ray absorption spectroscopy (XAS) on  $\text{CrO}_x/\text{MCM-41}$ , confirming that the reduction of  $\text{Cr}^{6+}$  occurs during the reaction.<sup>91</sup> Specifically, they identified  $\text{Cr}^{6+}\text{O}_4$  tetrahedra as the active species. These  $\text{Cr}^{3+}\text{O}_6$  octahedra were formed after reduction, which were considered to be less active. It was shown that  $\text{CO}_2$  could re-oxidise the Cr, which suggests that the redox cycle between  $\text{Cr}^{6+}$  and  $\text{Cr}^{3+}$  is an important process during the reaction. Yi *et al.* discriminated between isolated  $\text{Cr}^{6+}$  and polymeric  $\text{Cr}^{6+}$ , finding that after reduction, isolated  $\text{Cr}^{3+}$  was more active than polymeric  $\text{Cr}^{3+}$ . This underlines the importance of Cr dispersion in these catalysts.<sup>259</sup>

In a more detailed examination of  $\text{Cr}_2\text{O}_3/\text{SBA-1}$ , the relationship between the physicochemical properties of the catalyst and the observed activity were explored.<sup>85</sup> Michorczyk *et al.* found a strong positive correlation between the initial propene yield and the reducibility of the catalyst, specifically the  $\text{H}_2$  consumption. *In situ* UV-vis measurements revealed that  $\text{Cr}^{6+}$  is rapidly reduced to  $\text{Cr}^{3+}$  or  $\text{Cr}^{2+}$  in the presence of  $\text{C}_3\text{H}_8$  under reaction conditions. The reaction proceeds through a Mars-Van Krevelen mechanism, *via* the  $\text{Cr}^{2+/3+}$  redox couple. Rapid deactivation, typical of  $\text{Cr}_2\text{O}_3$  catalysts, was observed, although the majority of the initial activity could be

recovered after regeneration in air. The remainder was ascribed to pore collapse and/or the formation of inactive Cr sites, although the loss of surface Cr sites through agglomeration was not considered.

Despite early reports that activated carbon (AC) was not a suitable support for  $\text{Cr}_2\text{O}_3$ , subsequent studies have shown that above 550 °C, the activity of  $\text{Cr}_2\text{O}_3/\text{AC}$  in the presence of  $\text{CO}_2$  was higher than in the DDH reaction.<sup>260</sup> The enhancement in propane conversion due to the presence of  $\text{CO}_2$  increased at higher temperatures (*i.e.*, above 600 °C), although this was chiefly due to propane dry reforming proceeding, generating CO and  $\text{H}_2$  rather than propene. While this  $\text{Cr}_2\text{O}_3/\text{AC}$  exhibited the highest STY of propene out of all  $\text{CrO}_x$ -based catalysts ( $21 \text{ mol}_{\text{C}_3\text{H}_6} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$ , Table 11, entry 9), it rapidly deactivated on-stream and due to the support being carbonaceous, cannot be regenerated using air. This severely limits the utility of this catalyst.

Zeolites have also been considered as catalyst supports for  $\text{Cr}_2\text{O}_3$ . Zhang *et al.* prepared  $\text{CrO}_x/\text{Na-ZSM-5}$  *via* incipient wetness.<sup>261</sup> Although the initial conversion and selectivity was high (48% and 86%, respectively) (Table 11, entry 5), the catalysts deactivated rapidly and the reaction conditions were such that the STY was only  $2.5 \text{ mol}_{\text{C}_3\text{H}_6} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$  at 550 °C with a  $\text{CO}_2:\text{C}_3\text{H}_8$  ratio of 2. Zhu *et al.* investigated a range of MFI supports, including silicalite-1 and H[B]MFI.<sup>262</sup>  $\text{CrO}_x/\text{H[B]MFI}$  was found to be the most active catalyst, giving a STY of  $4.7 \text{ mol}_{\text{C}_3\text{H}_6} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$  at 600 °C with a  $\text{CO}_2:\text{C}_3\text{H}_8$  of 1 (Table 11, entry 15). Although the as-prepared catalyst exhibited typically poor stability for Cr catalysts, steam treating the catalyst resulted in a marked improvement. After 60 h on-stream, the as-prepared catalyst retained only 25% of its initial conversion, while the steam treated catalyst retained *ca.* 74%. The authors ascribed the effect to stabilised  $\text{Cr}^{3+}$  formed in the steam treatment. Presumably the reduction of  $\text{Cr}^{6+}$  during the reaction results in an inactive or less active  $\text{Cr}^{3+}$  species. It should also be noted that the as-prepared catalyst was initially almost twice as active as the steam treated catalyst, which leaves the possibility that at higher conversions, increased coke formation may have occurred which would exaggerate the deactivation compared to the steam treated catalyst. Ideally such stability comparisons would be made at isoconversion, however this discovery is one of only a few that shows improved stability on-stream. Recently, Michorczyk *et al.* prepared a Cr- $\beta$ -zeolite and investigated the effect of dealumination, which clearly elucidated the effect of acidity on the catalytic performance.<sup>263</sup> It was reported that the dealuminated catalyst, Cr-SiBeta, exhibited significantly higher propene yields (up to 27%), compared to the Al-containing catalyst, Cr-AlBeta (2%). The presence of acid sites in the Cr-AlBeta catalyst resulted in cracking pathways that led to increased production of methane and ethene. Moreover, the Cr-Albeta catalyst performed less well in the presence of  $\text{CO}_2$  than in the DDH reaction. This was explained by the strong adsorption of  $\text{CO}_2$  on the catalyst, similar to the inhibition observed over  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  catalysts. The stability of the dealuminated catalyst was also improved compared with Cr-Albeta, but significant loss



in activity was observed over the 4 h reaction. In considering the redox properties of the catalysts in this work, and their previous investigations, the authors also identified a strong correlation between the  $H_2$  consumption from  $H_2$ -TPR studies and the reported propene yield, as shown in Fig. 10.

While the majority of investigations on ODH- $CO_2$   $Cr_2O_3$  catalysts have focused on support modifications, the addition of a promotor has also been shown to be beneficial. Yun *et al.* demonstrated that the addition of 0.5 wt% Ni to a 10 wt%  $CrO_x$ /SBA-15 catalyst increased the propane and  $CO_2$  conversion, as well as the on-stream stability.<sup>264</sup> After 1 h on-stream, the Ni-promoted catalyst was 50% more active and the conversion and selectivity was almost maintained over 12 h on-stream. In contrast, the less active unpromoted catalyst retained only half of the initial activity over the same time period. Using three-stage  $H_2$ -TPR experiments (where the catalyst is reduced twice under  $H_2$  and then re-oxidised in  $CO_2$  before the final  $H_2$ -TPR program), the authors showed that the addition of Ni facilitated the re-oxidation of Cr during the reaction. This is consistent with previously reported mechanisms of deactivation over Cr-based catalysts, although coking is also often reported to cause deactivation. Interestingly, the promoted catalyst was marginally more prone to coking. This strongly suggests that overreduction of active Cr sites is the key deactivation mechanism over these catalysts. There is a lot of potential to develop promoted Cr catalysts that could enhance the redox activity of the catalyst; precious metals including Pd and Pt are often supported on reducible supports for this purpose.<sup>265</sup> Crucially, it was found that above 0.5 wt% Ni, propane reforming was prevalent, which underlines the importance of appropriate loadings of promoters.

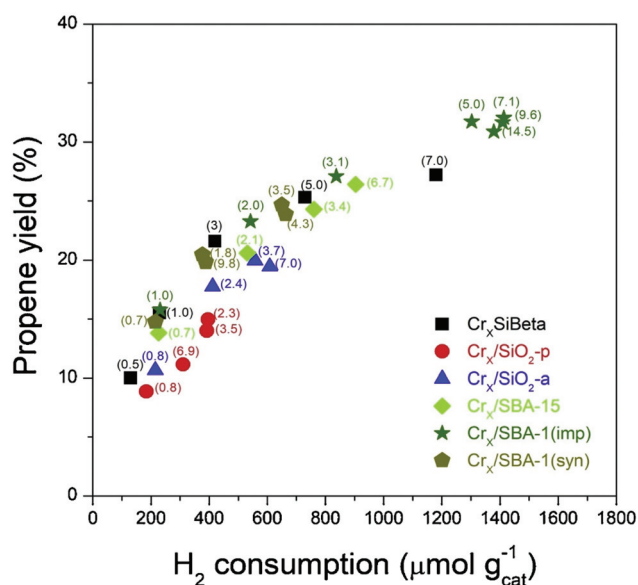


Fig. 10 The relationship between the reducibility of various supported Cr catalysts, and the reported propene yield. Reproduced from ref. 263 with permission from Elsevier.

O'Brien *et al.* investigated the effect of a Ru promoter to a 10 wt%  $CrO_x/SiO_2$  catalyst. Consistent with Yun *et al.* it was shown that the propene formation rate was increased. A 1 wt% Ru loading was optimal and doubled the activity. Interestingly, this is approximately the same molar ratio reported as the optimum by Yun *et al.* for Ni-promoted  $CrO_x/SBA-15$  (Table 11, entry 14).<sup>264</sup> Another similarity was the propensity of reforming to dominate at high loadings (>1 wt%). The enhanced stability seen in Ni-promoted Cr catalysts was not observed in this work and the activity could not be fully recovered after regeneration. Consequently, aggregation of Cr species was suggested as an additional deactivation mechanism in addition to coke formation and overreduction of Cr. Rather than aid Cr re-oxidation in a one-step oxidative dehydrogenation, the authors concluded that the Ru promotes the RWGS reaction, which removes  $H_2$  and increases the equilibrium conversion of propane. However, the results of three-stage  $H_2$ -TPR reactions indicated that Cr can be more easily oxidised in the presence of Ru, which suggests that Ru can participate in a similar role as Ni-promoted Cr catalysts.

Overall supported chromium oxide catalysts represent one of the most active classes of ODH- $CO_2$  catalysts, with STY values in the range of 2–22  $\text{mol}_{C_3H_6} \text{ kg}_{cat}^{-1} \text{ h}^{-1}$ . The role of the support is simply to maximise the active  $Cr^{6+}$  surface area, rather than add any chemical functionality, hence this is the reason why chemically-unreactive supports such as  $SiO_2$  and activated carbon yield the most active  $CrO_x$  catalysts. The most significant barrier to commercial application is the poor on-stream stability exhibited by all chromium-based catalysts. While incremental improvements in the activity of Cr catalysts have been reported since their initial discovery, significant advances in catalyst stability have been relatively few.

## 6.2. Gallium-based ODH- $CO_2$ catalysts

Gallium oxide is the second most widely studied element for ODH- $CO_2$  catalysis, owing to its successful application for DDH, as discussed above. It was first identified as an efficient DDH catalyst in 1988 in the context of dehydrocyclodimerisation,<sup>268</sup> but since the turn of the century it has been the subject of more intensive research.

The first application of gallium catalysts in ODH- $CO_2$  was carried out using ethane as a substrate.<sup>269</sup> Although ODH- $CO_2$  using ethane is beyond the scope of the current review, it is instructive to consider the catalytic activity of  $Ga_2O_3$  in the early reports from Nakagawa *et al.*  $TiO_2$ ,  $Al_2O_3$  and  $SiO_2$  were selected as catalyst supports for  $Ga_2O_3$  and it was found that  $Ga_2O_3/TiO_2$  was the most active catalyst.<sup>270</sup> Additionally, it was found that co-feeding steam was beneficial to maintain high activity, although rapid deactivation was still apparent. Consistent with the literature on supported  $CrO_x$  catalysts, the addition of  $CO_2$  to  $Ga_2O_3/Al_2O_3$  was shown to be detrimental to ethene yield. This strongly suggests that  $Al_2O_3$  is the origin of the inhibition observed in  $CrO_x/Al_2O_3$  catalysts.<sup>248</sup> It is known that the balance of acid and base sites is important to mediate the activation of the alkane and the desorption of the alkene. The addition of  $CO_2$  is likely to result in competitive





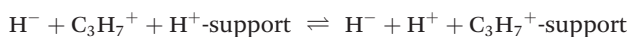
Table 12 Catalytic performance of selected gallium-based catalysts for ODH-CO<sub>2</sub>

Entry	Catalyst	T/°C	CO <sub>2</sub> /C <sub>3</sub> H <sub>8</sub>	WHSV/g <sub>C<sub>3</sub>H<sub>8</sub></sub> g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	X <sub>C<sub>3</sub>H<sub>8</sub></sub> /%	S <sub>C<sub>3</sub>H<sub>6</sub></sub> /%	STY/mol <sub>C<sub>3</sub>H<sub>6</sub></sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	Ref.
1	Ga <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>	500	2	0.15	49.7	91.7	1.4	274
2	β-Ga <sub>2</sub> O <sub>3</sub>	500	2	0.15	23	94	0.7	271
3	Ga <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>	550	5	1.2	19	91.6	4.3	273
4	CrO <sub>x</sub> /β-Ga <sub>2</sub> O <sub>3</sub>	550	7	0.89	33.7	84.7	5.3	272
5	Ga <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	600	2	0.30	26	94	1.5	114
6	GaN/SiO <sub>2</sub>	600	2	1.8	31	93	11	276
7	Ga <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>	600	2	0.15	49.7	91.7	1.6	275
8	Ga <sub>2</sub> O <sub>3</sub> /ZSM-48	600	2	0.30	52.6	42.2	1.5	113

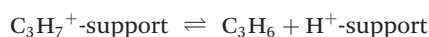
T = reaction temperature; CO<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> = molar ratio of CO<sub>2</sub>:C<sub>3</sub>H<sub>8</sub> in the reaction, X<sub>C<sub>3</sub>H<sub>8</sub></sub> = initial propane conversion, S<sub>C<sub>3</sub>H<sub>6</sub></sub> = initial propene selectivity, STY = space time yield.

adsorption on basic sites, and this may result in longer surface lifetimes of alkyl intermediates, resulting in undesirable side-reactions.

Zheng *et al.* investigated ODH-CO<sub>2</sub> of propane over different polymorphs of gallium oxide and found that β-Ga<sub>2</sub>O<sub>3</sub> (Table 12, entry 2) was the most active, even outperforming Cr<sub>2</sub>O<sub>3</sub> at 500 °C.<sup>271</sup> Interestingly, this was not the case for the DDH reaction, where Cr<sub>2</sub>O<sub>3</sub> was the most active catalyst. However, the activity of all the Ga<sub>2</sub>O<sub>3</sub> polymorphs was lower in the presence of CO<sub>2</sub>. Subsequently, Michorczyk *et al.* investigated CrO<sub>x</sub>/Ga<sub>2</sub>O<sub>3</sub> for ODH-CO<sub>2</sub> and showed that at elevated temperatures (>570 °C), the addition of CO<sub>2</sub> is beneficial (compared to DDH).<sup>272</sup> At 550 °C, the STY was 5.3 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. A non-oxidative reaction pathway was suggested to proceed *via* an initial heterolytic dissociation of propane, form a gallium alkoxide and a gallium hydride species. Then proton abstraction occurs, leaving H<sup>+</sup> and H<sup>-</sup> on the surface of the gallium oxide and propene. The abstraction of the second H atom is slow and considered rate-limiting. The authors suggested that this can be enhanced by a secondary equilibrium involving the surface migration of a surface proton. This equilibrium is as follows:



This results in the formation of propene *via*:



These reactions are facilitated by Lewis acid sites, specifically tetrahedral Ga ions. The role of CO<sub>2</sub> in ODH-CO<sub>2</sub> is to assist the above equilibrium by removing H<sub>2</sub> *via* the RWGS reaction.

The effect of the support was closely examined for propane ODH-CO<sub>2</sub> by Xu *et al.*<sup>114</sup> It was found that Ga<sub>2</sub>O<sub>3</sub> supported on TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub> exhibited high activity, while SiO<sub>2</sub> and MgO resulted in poorer performing catalysts. However, consistent with previous reports it was found that the addition of CO<sub>2</sub> to the reaction feed was detrimental when Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> were used as supports and higher propane conversion was observed when using lower CO<sub>2</sub>:C<sub>3</sub>H<sub>8</sub> ratios. Despite this, the propene yield was highest over Ga<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> in ODH-CO<sub>2</sub>, the

equivalent of 1.5 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> (Table 12, entry 5). The low activity of Ga<sub>2</sub>O<sub>3</sub>/MgO and Ga<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> was ascribed to the absence of medium and strong acid sites. In addition to the acid-base properties of the support, the authors considered the interaction between the Ga and the support to be of importance. In the Ga<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> catalyst, a significant proportion of the Ga (45%) was reduced. This catalyst exhibited the highest propane conversion, but with a propene selectivity of 73% it did not result in the highest propene yield.

Although the addition of Al<sub>2</sub>O<sub>3</sub> to ODH-CO<sub>2</sub> catalysts is typically not beneficial,<sup>114,273</sup> Chen *et al.* investigated spinel-type Ga<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> mixed oxides and showed that they can function as stable catalysts.<sup>274,275</sup> At 600 °C, although the initial propane conversion was similar for DDH and ODH-CO<sub>2</sub>, after 8 h on-stream the stability of the catalyst was markedly improved in the presence of CO<sub>2</sub>, where Ga<sub>8</sub>Al<sub>2</sub>O<sub>15</sub> retained 66% of its initial activity, compared to just 44% in the absence of CO<sub>2</sub>. The origin of stability was linked to the low rate of coking associated with the spinel catalyst. Using NH<sub>3</sub>-TPD analysis, the authors concluded that weak Lewis acid sites were conducive to high activity. These acid-base properties most likely contribute to the enhanced stability as well; it is known that stronger acid sites promote oligomerisation pathways that produce coke. While many previous studies on ODH-CO<sub>2</sub> have shown Al<sub>2</sub>O<sub>3</sub> to be detrimental to catalyst performance (compared with DDH activity), this investigation highlights the sensitivity of the catalyst performance to the structure of the surface, and the acid-base properties therein.

Ren *et al.* studied the effect of acidity and pore geometry in Ga<sub>2</sub>O<sub>3</sub> supported on ZSM-48 and ZSM-5.<sup>113</sup> At 600 °C, the most active catalyst, Ga<sub>2</sub>O<sub>3</sub>/ZSM-48 with a Si:Al ratio of 130, demonstrated a 22.2% propene yield, although the selectivity to propene was only 42% (Table 12, entry 8). Aromatics (including retained carbonaceous products) accounted for 40% of the converted carbon. An increase in the Si:Al ratio resulted in an increase in propene selectivity on both H-ZSM-5 and ZSM-48 supports. Compared with DDH, in ODH-CO<sub>2</sub> the propane conversion was slightly higher, but the propene selectivity was lower, resulting in a marginally decreased propene yield. The increased performance of Ga<sub>2</sub>O<sub>3</sub>/ZSM-48 was attributed to the abundance of weak and medium strength acid sites.



Recently, it has been shown that gallium nitride can function as a highly active catalyst for ODH-CO<sub>2</sub> when supported on porous SiO<sub>2</sub>.<sup>276</sup> At 600 °C with a CO<sub>2</sub>:C<sub>3</sub>H<sub>8</sub> ratio of 2, the catalyst exhibited a propane conversion of 31% and a propene selectivity of 93%, equivalent to a STY of 11 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> (Table 12, entry 6), the highest value reported for any Ga-based catalyst. Although some deactivation was observed (*ca.* 83% of initial steady state activity retained after 8 h on-stream), the catalysts can be considered to be amongst the most stable reported to date. While the authors did not investigate the reaction mechanism of the supported GaN, it is instructive to consider the observed induction period in each catalyst whereby the propane conversion increases over the first 1–2 h; for the most active catalyst it increases from 20% to 30% in this timeframe. A similar induction period has been observed over BN catalysts for the ODH-O<sub>2</sub> of propane by Hermans *et al.*, amongst others,<sup>196,202,204</sup> which was ascribed to the oxidation of BN to form active B-OH groups. It is reasonable to suggest that a similar oxidation/hydroxylation of the GaN surface occurs here, although it is unclear how, or even if, CO<sub>2</sub> could facilitate this *in situ*. XPS of the as-prepared samples showed a large O 1s signal, but this was ascribed to adsorbed H<sub>2</sub>O.

Overall, Ga<sub>2</sub>O<sub>3</sub> can be considered to be moderately active for ODH-CO<sub>2</sub>, with reasonable propene yields, but generally poor stability. In most cases, the inclusion of CO<sub>2</sub> is not beneficial for the reaction. Compared with CrO<sub>x</sub>, Ga typically results in lower propene yield and comparable stability. The recent breakthrough regarding GaN, however, is very noteworthy. With a similar STY to the most active CrO<sub>x</sub> catalysts and relatively good on-stream stability at high conversion (*ca.* 30%), this new class of Ga catalysts has real potential. Future research into GaN catalysts should seek to understand the reaction mechanism in order to identify the active sites and improve catalyst performance further.

### 6.3. Metal oxide based ODH-CO<sub>2</sub> catalysts

In addition to chromium and gallium, a selection of other oxide catalysts, mostly of transition metals, have been explored for their ODH-CO<sub>2</sub> activity. This section details the most significant advances made to date with respect to these other metal oxides.

Bulk and supported iron oxides have been investigated by Michorczyk *et al.*<sup>277</sup> Unsupported Fe<sub>2</sub>O<sub>3</sub> exhibited reasonable

activity at 600 °C when using a CO<sub>2</sub>:C<sub>3</sub>H<sub>8</sub> ratio of 5, with a propene yield of 7.5%. The activity was four times higher than in the absence of CO<sub>2</sub>, and the propene selectivity increased from 84 to 92.5%. The dispersion of Fe<sub>2</sub>O<sub>3</sub> on activated carbon significantly improved the conversion of propane from 8.2 to 29.7%, which corresponds to a STY of 16.1 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> (Table 13 entry 7). In contrast, using Al<sub>2</sub>O<sub>3</sub> as a support for the Fe<sub>2</sub>O<sub>3</sub> inhibited the performance of the catalyst. The reaction mechanism was concluded to proceed *via* a redox pathway, whereby the lattice oxygen associated with the iron oxide directly participates in the reaction.

A 5 wt% ZnO/H-ZSM-5 catalyst was investigated by Ren *et al.* using a broad range of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios (60, 120, 160, 201 and 242) at 600 °C.<sup>278</sup> While all of the prepared catalysts exhibited some activity (with conversion ranging from 40–86%), the highest propene yield was observed over ZnO/H-ZSM-5 (160), which was 46.8% (Table 13, entry 3). In each catalyst, the main competing pathway was to aromatics, which is consistent with the use of ZSM-5 in aromatisation catalysis.<sup>247</sup> It was recognised that CO<sub>2</sub> both promotes the RWGS reaction over the supported ZnO catalysts, but also blocks active sites. The stability was improved in the presence of CO<sub>2</sub> (compared to DDH); *ca.* 74% of the original activity was retained after 10 h on-stream, which is relatively good compared to Ga- and Cr-based catalysts.

Indium oxide and various mixed-metal oxides containing In have been considered as ODH-CO<sub>2</sub> catalysts in recent years. Chen *et al.* initially demonstrated that In<sub>2</sub>O<sub>3</sub> was active, but also showed that the performance is improved as a binary oxide of In<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub>.<sup>279</sup> Specifically, In<sub>20</sub>Al<sub>80</sub>O<sub>x</sub> exhibited the highest propene yield under the reaction conditions used (600 °C, CO<sub>2</sub>:C<sub>3</sub>H<sub>8</sub> = 4:1), which was *ca.* 27% (Table 13, entry 5). Interestingly, each of the mixed metal catalysts exhibited an induction period over the first 3 h, followed by moderate deactivation. In contrast, Al<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> alone deactivated much more rapidly on-stream and without an induction period. The origin of this induction period was found to be reduction of In<sub>2</sub>O<sub>3</sub> to In<sup>0</sup> nanoclusters, which suggests the active structure is more of a supported nanoparticle type catalyst than a mixed-metal oxide. Chen *et al.* also considered a wide range of secondary metal oxides for this reaction, using sol-gel or co-precipitation to prepare In<sub>2</sub>O<sub>3</sub>–MO<sub>x</sub>, where x = Al, Zn, Zr, Ti, Fe, Mg, Si and Ce.<sup>280</sup> It was shown that the In<sub>2</sub>O<sub>3</sub>–

**Table 13** The catalytic performance of selected metal oxide-based catalysts for ODH-CO<sub>2</sub>

Entry	Catalyst	T/°C	CO <sub>2</sub> /C <sub>3</sub> H <sub>8</sub>	WHSV/g <sub>C<sub>3</sub>H<sub>8</sub></sub> g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	X <sub>C<sub>3</sub>H<sub>8</sub></sub> /%	S <sub>C<sub>3</sub>H<sub>6</sub></sub> /%	STY/mol <sub>C<sub>3</sub>H<sub>6</sub></sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	Ref.
1	10 mol%Fe <sub>2</sub> O <sub>3</sub> –CeO <sub>2</sub>	550	1	0.59	18	46	1.0	287
2	8 wt% In <sub>2</sub> O <sub>3</sub> /H-ZSM-5	580	4	1.2	13	81	2.5	282
3	5 wt% ZnO/H-ZSM-5	600	2	0.30	68	47	2.0	278
4	V-MCM-41	600	4	1.0	58	90	11	286
5	In <sub>2</sub> O <sub>3</sub> –Al <sub>2</sub> O <sub>3</sub>	600	4	0.15	35	75	0.81	279
6	In <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	600	4	0.15	14	80	0.36	281
7	Fe <sub>2</sub> O <sub>3</sub> /AC	600	4.9	2.77	3	83	16	277

T = reaction temperature; CO<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> = molar ratio of CO<sub>2</sub>:C<sub>3</sub>H<sub>8</sub> in the reaction, X<sub>C<sub>3</sub>H<sub>8</sub></sub> = initial propane conversion, S<sub>C<sub>3</sub>H<sub>6</sub></sub> = initial propene selectivity, STY = space time yield. AC = activated carbon.



Al<sub>2</sub>O<sub>3</sub> combination was the most active, due in part to the high dispersion of In in this particular catalyst. Further investigation into the composition of the support revealed that compared with ZrO<sub>2</sub> and SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> was the most effective support for In<sub>2</sub>O<sub>3</sub>, although ZrO<sub>2</sub> was also active.<sup>281</sup> The basicity of the In/ZrO<sub>2</sub> system was suggested to promote the RWGS reaction, which in turn boosted the ODH-CO<sub>2</sub> activity. This conclusion was supported by the substantial increase in the activity observed in ODH-CO<sub>2</sub> compared with DDH. Tian *et al.* recently investigated In/H-ZSM-5.<sup>282</sup> At 580 °C and a CO<sub>2</sub>:C<sub>3</sub>H<sub>8</sub> ratio of 4:1, the highest propene yield was 10%. Although the propane conversion was similar without In present, the selectivity was significantly increased from 28% for H-ZSM-5 to 81% for 4 wt% In/H-ZSM-5 (Table 13, entry 2).

Supported vanadia catalysts have also been considered in ODH-CO<sub>2</sub> having been widely applied in various reactions, including propane ODH-O<sub>2</sub>,<sup>4</sup> toluene oxidation<sup>283</sup> and formaldehyde oxidation.<sup>284</sup> Vanadia catalysts for ODH-CO<sub>2</sub> were first reported by Nakagawa *et al.* and in this early study, supported vanadia was found to outperform Ga<sub>2</sub>O<sub>3</sub>.<sup>249</sup> Despite this, few studies have been reported since.<sup>285</sup> Notably, Ascoop *et al.* investigated the role of CO<sub>2</sub> in the reaction over composite WO<sub>x</sub>-VO<sub>x</sub>/SiO<sub>2</sub> catalysts. Using D<sub>2</sub> as a co-feed, it was shown that 45% of the resultant water contained D<sub>2</sub>O. This confirmed a Mars-Van Krevelen mechanism as well as a two-step DDH + RWGS mechanism proceeds over this catalyst. It was found that CO<sub>2</sub> could partially re-oxidise the catalyst and that coke formation was significantly suppressed in the presence of CO<sub>2</sub>. Han *et al.* examined a range of VO<sub>x</sub> loadings using an MCM-41 as a support.<sup>286</sup> The most active catalyst, 6.8 wt% VO<sub>x</sub>/MCM-41, exhibited an initial propene yield of 51% at 600 °C with a CO<sub>2</sub>:C<sub>3</sub>H<sub>8</sub> ratio of 4:1. However, the catalyst retained only 65% of its initial activity after 2 h on-stream. The initial STY of this catalyst was 10.7 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> (Table 13, entry 4), which is amongst the most active reported to date, but requires significant improvements to its on-stream stability.

Tsilomelekis and Wang recently investigated mixed metal oxides comprising Fe and Ce for the ODH-CO<sub>2</sub> reaction. It was found that 10 mol% Fe in CeO<sub>2</sub> exhibited the highest propene yield. The propene selectivity of this catalyst was *ca.* 45% at 550 °C with a propane conversion of *ca.* 18%. The major side-reactions observed were dry reforming and cracking. They showed that reforming pathways were more prevalent at higher CO<sub>2</sub>:C<sub>3</sub>H<sub>8</sub> ratios, such as 2.5:1 and 5:1. However, the catalysts were relatively stable on-stream over 20 h, retaining 80%

of their initial activity. Despite the low selectivity, the Fe-CeO<sub>2</sub> catalysts exhibited a comparable STY to supported In<sub>2</sub>O<sub>3</sub> (Table 13) and some Ga<sub>2</sub>O<sub>3</sub> catalysts (Table 12).

#### 6.4. Supported nanoparticle based ODH-CO<sub>2</sub> catalysts

Despite forming an active component in various industrial DDH processes and being extensively reported in the academic literature for DDH, the number of studies carried out over Pt-based catalysts for ODH-CO<sub>2</sub> is comparatively low. This is also true of other noble metals such as Pd, Au and Ru, where only a handful of studies are available. In this section, the available literature on supported nanoparticle (NP) catalysts, including noble metals, is discussed.

The earliest report of utilising a supported metal NP in ODH-CO<sub>2</sub> was by Guo *et al.* in 2005 who compared Ga and Re supported on H-ZSM-5 (Table 14, entry 4).<sup>247</sup> It was shown that at 550 °C, the addition of CO<sub>2</sub> inhibited the propane conversion significantly and did not greatly affect the selectivity to propene (5.7%). As described above, aromatisation tends to be the dominant pathway when H-ZSM-5 is used.

Supported gold catalysts, which are widely used as catalysts for oxidation reactions<sup>288</sup> including the epoxidation of propene,<sup>289</sup> were studied by Tóth *et al.* When Au NPs supported on MgO, ZnO or Al<sub>2</sub>O<sub>3</sub> were investigated over a broad temperature range (500–750 °C), only Au/ZnO exhibited reasonable catalytic activity. The propene selectivity was 56% at 50% conversion at 600 °C. The Au/ZnO material was shown to be very unreactive towards propene and evidence for propane activation at 25 °C was found. Despite this promising initial data, Au NP catalysts have not been investigated further.

Gomez *et al.* investigated various mono- and bi-metallic NP catalysts using CeO<sub>2</sub> as a support at a reaction temperature of 650 °C and a CO<sub>2</sub>:C<sub>3</sub>H<sub>8</sub> ratio of 1:1 (Table 14, entries 2 and 3).<sup>21,290</sup> Among the wide range of catalysts tested were Ni<sub>1</sub>, Fe<sub>1</sub> and Fe<sub>3</sub>-Ni<sub>1</sub> (where the subscript number indicates the molar ratio). While Ni<sub>1</sub> was active mostly for dry reforming to CO + H<sub>2</sub>, Fe<sub>1</sub> was inactive. However, Fe<sub>3</sub>-Ni<sub>1</sub> exhibited much higher selectivity towards propene. *In situ* XAS measurements revealed that under reaction conditions Fe was oxidised and Ni was metallic. While the overall performance of Fe<sub>3</sub>-Ni<sub>1</sub> was moderate (58% selectivity to propene at 2.7% propane conversion, equivalent to a STY of 3.9 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>), the findings demonstrate the sensitivity of reaction pathways to the nano-structure of the catalyst and suggest further optimisation is possible. Subsequent studies on Fe-Co and Fe-Pd catalysts

**Table 14** Comparison of selected literature supported NP and metal carbide catalysts for ODH-CO<sub>2</sub>

Entry	Catalyst	<i>T</i> /°C	CO <sub>2</sub> /C <sub>3</sub> H <sub>8</sub>	WHSV /g <sub>C<sub>3</sub>H<sub>8</sub></sub> g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	<i>X</i> <sub>C<sub>3</sub>H<sub>8</sub></sub> /%	<i>S</i> <sub>C<sub>3</sub>H<sub>6</sub></sub> /%	STY/mol <sub>C<sub>3</sub>H<sub>6</sub></sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	Ref.
1	Pd/CeZrAlO <sub>x</sub>	500	1	3.3	9.5	93	4.9	291
2	Fe <sub>3</sub> -Ni <sub>1</sub> /CeO <sub>2</sub>	550	1	11.8	2.7	58.2	3.9	21
3	Co <sub>3</sub> -Pd <sub>1</sub> /CeO <sub>2</sub>	550	1	11.8	2.8	25.8	1.8	290
4	Re/H-ZSM-5	550	2.3	0.70	57.6	5.65	0.48	247
5	Mo <sub>2</sub> C	550	0.2	0.96	0.5	99	0.11	295

*T* = reaction temperature; CO<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> = molar ratio of CO<sub>2</sub>:C<sub>3</sub>H<sub>8</sub> in the reaction, *X*<sub>C<sub>3</sub>H<sub>8</sub></sub> = initial propane conversion, *S*<sub>C<sub>3</sub>H<sub>6</sub></sub> = initial propene selectivity, STY = space time yield.



revealed similar trends, whereby the addition of Fe to Co or Pd boosted the selectivity to propene compared with the corresponding monometallic catalyst. However, in all cases the dry reforming reaction competed with the dehydrogenation pathway, significantly limiting the propene selectivity.<sup>290</sup>

Nowicka *et al.* carried out a detailed investigation into Pd/CeZrAlO<sub>x</sub> catalysts.<sup>291</sup> It was shown that CO<sub>2</sub> dissociation on the catalyst support was facilitated by the presence of Pd. At 500 °C the catalyst achieved 9.5% conversion and 93% selectivity to propene. Although the STY was 4.9 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, (Table 14, entry 1) the reaction temperature was 500 °C, which is low for ODH-CO<sub>2</sub> catalysts. Above this temperature, the selectivity to propene rapidly drops and methane and carbon monoxide production increase. It should also be noted that propene selectivity was calculated based on observed products, rather than propane consumption and therefore the contribution of dry reforming was not measured.

Metal carbides have been intensively investigated in recent years for a broad range of reactions and are often described as having properties analogous to precious metals.<sup>292–294</sup> To date, there have been two reports of metal carbides catalysing ODH-CO<sub>2</sub>, both of which focus on Mo<sub>2</sub>C.<sup>295,296</sup> It was found that in addition to dehydrogenation, hydrogenolysis and reforming played important roles in the reaction network. Overall, the performance of the carbide catalysts was poor compared to typical metal oxide or supported nanoparticle catalysts (Table 14, entry 5).

The number of studies on supported nanoparticle catalysts for ODH-CO<sub>2</sub> are relatively few and those available indicate that this field of research has great potential. The major challenge is in understanding and inhibiting side-reactions such as reforming, which are known to proceed over this class of catalyst, unlike in Cr- and Ga-based catalysts. Careful consideration of the nanostructure and composition has shown that the selectivity can be readily tuned to favour different pathways, and further investigation in this area may well be able to harness the high activity of supported nanoparticles as well as favour dehydrogenation pathways.

Despite the fact that ODH-CO<sub>2</sub> of light alkanes has been known for over twenty years, catalyst design has largely been limited to a handful of metal oxide catalysts, namely chromia and gallia. The most promising of these catalysts are supported metal oxides, which typically result in high initial propene yields. However, all catalysts suffer from rapid deactivation on-stream, which is typically attributed to coke formation blocking active sites. However, few investigations have studied the long-term stability of the catalyst beyond 12 h on-stream. In many cases, the catalyst can be regenerated periodically, by burning off the coke using O<sub>2</sub>. As discussed above, catalyst regeneration is commonplace in commercial DDH processes and therefore isn't necessarily a barrier to commercialisation. However, the best STYs reported are, with few exceptions, in the range of 5–10 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, whereas for the DDH reaction, values over 100 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> are possible. As a result, further advances in the activation of propane over ODH-CO<sub>2</sub> catalysts are required. Despite dozens of reports over

several decades on Cr- and Ga- based catalysts, the improvements in catalyst performance have been incremental. The knowledge gained from these studies on the importance of reducibility and the balance of acid and base sites should be applied to supported NP catalysts, which are a promising and somewhat neglected category of ODH-CO<sub>2</sub> catalyst.

## 7. Oxidative dehydrogenation with nitrous oxide

O<sub>2</sub> and CO<sub>2</sub> are currently the most commonly reported oxidants in the oxidative dehydrogenation of propane. However, other oxidants have also been shown to be feasible. Sulfur dioxide and halogen-based compounds have largely been ignored in recent decades due to their corrosive properties, while H<sub>2</sub>O<sub>2</sub> has had its commercialisation deferred due to difficulties in its synthesis.<sup>297</sup> Another relevant oxidant, however, is N<sub>2</sub>O. It should be noted that N<sub>2</sub>O is a greenhouse gas which has a global warming potential approximately 310 times higher than that of CO<sub>2</sub>.<sup>298,299</sup> Therefore, processes that remove N<sub>2</sub>O gas from the atmosphere are highly desirable. The industrial sector produces N<sub>2</sub>O as a by-product from various processes, including nitric and adipic acid production as well as fossil fuel combustion sources which make up a total of 15% of anthropogenic sources.<sup>298</sup> Many production plants will have N<sub>2</sub>O abatement in place already, so the possibility for flowing propane through this process exists. Despite this, research into the ODH-N<sub>2</sub>O reaction of propane is rather limited, mostly due to the cost of N<sub>2</sub>O and product dilution in N<sub>2</sub>. Furthermore the research that does exist is reserved for elucidating structure–activity relationships, which can be used to better understand the ODH reaction in general.<sup>300</sup>

### 7.1. Fe-Zeolite based ODH-N<sub>2</sub>O catalysts

In 1998 Panov *et al.*<sup>301</sup> reported a new type of O species observed in Fe-ZSM-5 when it was exposed to N<sub>2</sub>O. The species was referred to as α-oxygen and is able to perform highly selective dehydrogenation and oxidation reactions of hydrocarbons such as the oxidation of benzene to phenol, which occurred with nearly 100% selectivity at conversions of 97–98%. In addition, dehydrogenation of ethane and methane oxidation reactions are also possible using N<sub>2</sub>O. Panov further detailed the characteristics of α-oxygen. It is typically associated with isolated Fe ions or small complexes found within the zeolite's micropores, as opposed to the tetrahedral Fe ions within the crystal lattice, or the finely dispersed metal oxide phase of the zeolite surface. It has been suggested that this oxygen species could be useful in the oxidative dehydrogenation of propane.

Other examples of ZSM-5 modified catalysts on top of Fe include doping with metals such as Mn and Co.<sup>302</sup> The authors examined the selectivity, conversion and yield of propene of these three materials. While all three showed similar selectivity (between 70–80%), Fe-ZSM-5 was reported to exhibit the highest conversion and therefore best yield towards propene. The α-oxygen species is formed *via* the interaction





between  $\text{N}_2\text{O}$  and framework stabilised  $\text{Fe}^{2+}$  ions, resulting in the dissociation of  $\text{N}_2\text{O}$  and the formation of mono- and bi-nuclear  $\text{Fe}^{3+}\text{-O}^-$  species, ( $\alpha$ -oxygen). These  $\alpha$ -oxygen species react with propane by providing atomic oxygen, producing propanol, which is subsequently dehydrated to propene.<sup>303,304</sup> It is from this mechanism that the selectivity originates, because once the hydrocarbon's interaction with  $\alpha$ -oxygen is complete, the molecule would need to vacate the zeolite channel in order for a new  $\text{N}_2\text{O}$  molecule to enter and generate an new  $\alpha$ -oxygen site, therefore not allowing for immediate further oxidation.<sup>301</sup> It is also evident from this mechanism that coordination of oxygen to an  $\text{Fe}^{2+}$  species is required, and therefore does not occur on tetrahedral framework Fe species due to a lack of vacant sites in the Fe complex.<sup>303</sup>

By considering simply the activation of  $\text{N}_2\text{O}$ , Groen *et al.*<sup>305</sup> enhanced the activation by performing an alkaline treatment on Fe-ZSM-5, which increased the number of  $\text{Fe}^{2+}$  sites, decreased the amount of oligonuclear clusters and increased the porosity of the zeolite. The calcined catalysts were treated in 0.2 M NaOH for 2 h, before undergoing an ion-exchange in  $\text{NH}_4\text{NO}_3$  solution. Where the calcined Fe-ZSM-5 catalyst reached complete conversion of  $\text{N}_2\text{O}$  at 552 °C, the catalysts which had undergone alkaline treatment and subsequent ion-exchange reached total conversion at slightly under 527 °C. This increase in porosity and highly active Fe sites shows potential for the dehydrogenation reaction of propane, however little research effort has extended into this area.<sup>305,306</sup>

Further to this, Pérez-Ramírez *et al.*<sup>303,307</sup> reported highly active catalysts after the steam treatment of Fe-ZSM-5 zeolites, which produced an initial STY of 180  $\text{mol}_{\text{C}_3\text{H}_6} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$  (Table 15, entry 2) when carried out at 525 °C. This high productivity is ascribed to the generation of extra-framework Fe sites during the steam treatment.<sup>303,307,308</sup> However, this high productivity is hindered by a rapid deactivation, with the authors observing a minimum decrease in propene yield of ca. 3% over 3 h at 452 °C, and a maximum decrease in propene yield of ca. 12% over the same timescale at 525 °C. This rapid deactivation, which will be discussed further, is the most significant issue facing the use of  $\text{N}_2\text{O}$  as an oxidant to date.

The main deactivation pathway of this catalyst is ascribed to the build-up of carbonaceous deposits at the Brønsted acid sites in the zeolite pores, therefore blocking the pores and active Fe sites. It has been reported that blocking or removing the Brønsted acid sites lessens the impact of

deactivation.<sup>303,309</sup> Despite being the major deactivation pathway, compared to other zeolite examples, ZSM-5 shows significant resistance to deactivation, despite the finding that they produce more coke than other examples. This behaviour is attributed to the location of the coke formation, which occurs at Al-protonic sites, away from the extra-framework Fe-active sites.<sup>303</sup> However, the use of  $\text{N}_2\text{O}$  as an oxidant invariably leads to rapid deactivation despite the positive effect of the zeolite, when compared to other oxidants, such as  $\text{O}_2$ . Using a mixture of oxidant gases,  $\text{O}_2$  and  $\text{N}_2\text{O}$ , was reported to decrease the deactivation of Fe-ZSM-5 further *via* oxidising the carbon deposits.<sup>309</sup> The limitation of this being the inclusion of too much  $\text{O}_2$ , leads to overoxidation of the desired products and therefore lower selectivity towards propene. Bulánek *et al.* reported that a mixture of  $\text{N}_2\text{O}$  and  $\text{O}_2$  over a steam-treated Fe-ZSM-5 catalyst and found that with the inclusion of oxygen the conversion consistently increased; however, the selectivity consistently decreased (Table 15, entry 1).<sup>309</sup> The problem remains, that when comparing oxidant properties for the ODH reaction of propane,  $\text{N}_2\text{O}$  has a significant tendency for rapid deactivation.

In 2010, Kowalska-Kuś *et al.*<sup>310</sup> investigated the role of Brønsted acid sites in Fe-ZSM-5 and their effect on the ODH- $\text{N}_2\text{O}$  activity. It was found that in the presence of a high number of protonic sites, cracking and ODH reactions of propane occurred simultaneously, and would often lead to high selectivity towards total oxidation products. Conversely, removal of protonic sites *via* doping with sodium reduced the oxidative activity of the zeolite and modified the reaction to favour the ODH pathway. Subsequently, the propene would undergo further cracking reactions. Therefore, shorter contact times result in higher propene selectivity. This method led to propene selectivities higher than previously reported for this reaction, (over 80%), but the limitation of this approach is the significantly lowered conversion due to the lower oxidative activity of the zeolite.

It is clear that adjusting the acidity of the zeolite greatly influences the conversion and selectivity of the ODH- $\text{N}_2\text{O}$  reaction. As mentioned earlier, steam treatment has been found to increase the number of  $\text{Fe}^{2+}$  active sites. This, as well as dealuminating the zeolites, leads to a higher presence of weak and medium acid sites, which enhance selectivity towards propene.<sup>304,311</sup> Steam treatment was also found to increase stability towards coking in the zeolites.<sup>311</sup> With these methodologies implemented, Ates *et al.*<sup>311</sup> were able to produce a catalyst with a STY of 10  $\text{mol}_{\text{C}_3\text{H}_6} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$  (Table 15, entry 4).

**Table 15** Comparison of catalytic performance of selected catalysts for the ODH- $\text{N}_2\text{O}$  reaction

Entry	Catalyst	$T/^\circ\text{C}$	$\text{N}_2\text{O}/\text{C}_3\text{H}_8$	$\text{WHSV} / \text{g}_{\text{C}_3\text{H}_8} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	$X_{\text{C}_3\text{H}_8} / \%$	$S_{\text{C}_3\text{H}_6} / \%$	$\text{STY} / \text{mol}_{\text{C}_3\text{H}_6} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$	Ref.
1	FeH-MFI-1200-HT	450	1	3.0	64	29	12	309
2	Steam-activated Fe-ZSM-5	450	1	39.4	48	45	180	303
3	$\text{VO}_x/\text{MCM-41}$	475	1	—	—	—	29	313
4	Steam-activated Fe-ZSM-5	500	1	2.4	29.2	68.8	10	311
5	$\text{In}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide	600	4	0.15	43.6	63.1	6.8	316

$T$  = reaction temperature;  $\text{N}_2\text{O}/\text{C}_3\text{H}_8$  = molar ratio of  $\text{N}_2\text{O}:\text{C}_3\text{H}_8$  in the reaction,  $X_{\text{C}_3\text{H}_8}$  = initial propane conversion,  $S_{\text{C}_3\text{H}_6}$  = initial propene selectivity, STY = space time yield. Values next to element/phase is the loading in wt%.



In summary, while the ODH-N<sub>2</sub>O reaction is hindered significantly by its tendency to deactivate rapidly without the presence of O<sub>2</sub>, Fe-ZSM-5 as a catalyst is very resistant to deactivation and its use for the ODH-N<sub>2</sub>O reaction is contingent on several factors. The oxidation of extra-framework Fe<sup>2+</sup> sites to Fe<sup>3+</sup>-O<sup>-</sup> sites is a crucial step in the mechanism, and therefore producing a material with a large number of these sites would increase the yield of propene. The Brønsted acidity of the Fe-ZSM-5 zeolite both decreases the selectivity to propene, due to a high number of protonic sites leading to selectivity towards total oxidation, and increases the rate of deactivation, allowing for the generation of carbonaceous deposits which block the zeolite pores. The most promising materials currently are steamed Fe-ZSM-5, as the steam treatment has been found to produce more Fe<sup>2+</sup> sites and dealuminate the framework, causing an increase in weak and medium acid sites. With fewer strong protonic sites, the reaction mechanism shifts towards favouring the dehydrogenation of propane, therefore resulting in a consecutive propane dehydrogenation-propene cracking pathway which allows for a higher selectivity to propene with shorter contact times. Despite these advancements, recent research on Fe-ZSM-5 for ODH-N<sub>2</sub>O has been minimal due to their rapid deactivation, the high cost of N<sub>2</sub>O and the presence of N<sub>2</sub> in the product stream.

## 7.2. Other ODH-N<sub>2</sub>O catalysts

Other catalysts reported to be active for the ODH-N<sub>2</sub>O reaction of propane include supported vanadium oxides. In 2001 Kondratenko *et al.*<sup>312</sup> reported that VO<sub>x</sub>/γ-Al<sub>2</sub>O<sub>3</sub> was active for ODH of propane with O<sub>2</sub> and N<sub>2</sub>O and investigated the effect of vanadia loading. It was found that, similar to Fe-ZSM-5 catalysts, on replacing O<sub>2</sub> with N<sub>2</sub>O the overall activity of the catalyst decreased, but the selectivity increased. This trend was ascribed to the lower oxidising potential of N<sub>2</sub>O.

Further to this, DFT studies were carried out to elucidate the role of the oxidant in the ODH reaction.<sup>300</sup> These calculations first revealed that propene is formed *via* successive removal of two hydrogen atoms *via* a redox mechanism over VO<sub>x</sub> active sites. The active sites are reduced from V<sup>5+</sup> to V<sup>3+</sup> and V<sup>4+</sup> during hydrogen removal from the propane molecule, which then require re-oxidation before removal of a second hydrogen. The N<sub>2</sub>O was found to only oxidise V<sup>3+</sup>, whereas O<sub>2</sub> was able to oxidise both V<sup>3+</sup> and V<sup>4+</sup>. Upon re-oxidation of the VO<sub>x</sub> active sites with O<sub>2</sub>, peroxovanadates were formed; however these species were not formed with N<sub>2</sub>O as the oxidant. Peroxovanadates are highly active for the total oxidation of propane. The formation of these peroxovanadates is a key explanation for the more selective nature of N<sub>2</sub>O compared to O<sub>2</sub>. In the most active catalyst, the STY of VO<sub>x</sub>/MCM-41 was 29 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> (Table 15, entry 3), which is less than the most active steam-activated Fe-ZSM-5 catalysts, but more active than some reports over Fe-MFI catalysts.

In addition, V/γ-Al<sub>2</sub>O<sub>3</sub>, V/MCM-41, and V/amorphous SiO<sub>2</sub> catalysts have also been prepared and characterised in order to elucidate the structure activity relationships between the catalyst and the ODH-N<sub>2</sub>O reaction of propane.<sup>313–315</sup> It was found

that the selectivity for propene was lower over V/γ-Al<sub>2</sub>O<sub>3</sub>; a result which was ascribed to the acidic nature of the alumina support, over which dehydrogenated propene adsorbed to the support surface where it further oxidised to CO<sub>x</sub> species. This effect is less prominent on less acidic support surfaces such as SiO<sub>2</sub> and MCM-41.

The vanadia loading on the support materials was also found to influence the selectivity.<sup>312–314</sup> On the materials V/MCM-41, and V/SiO<sub>2</sub> materials, the nature and distribution of the V remained consistent up to a loading of *ca.* 5 wt%, above which three-dimensional V<sub>2</sub>O<sub>5</sub> clusters began to form, and these have unreactive bulk V sites. At lower loadings however, the support surface is more exposed, allowing for adsorption of propene and total oxidation. Therefore, a loading of *ca.* 5 wt% is optimal to get a high surface coverage, without forming three-dimensional clusters. Kondratenko *et al.* were able to achieve selectivities of over 90% at conversions limited to 2 and 10% with such materials.<sup>315</sup>

Finally, in 2010, Chen *et al.* reported the use of In<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> as a novel catalyst for the ODH-CO<sub>2</sub>.<sup>279</sup> In 2011 the same group reported the same catalyst's potential for the ODH-N<sub>2</sub>O reaction.<sup>316</sup> The activity of the In<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst shows a significant dependence on the concentration of In<sup>0</sup> in the material. The catalyst exhibited a low STY of 6.8 mol<sub>C<sub>3</sub>H<sub>6</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> (Table 15, entry 5). Despite this, the In<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst shows potential to surpass the more commonly researched Fe-zeolites in terms of stability. Whereas previous examples of Fe-zeolites have displayed significant deactivation over 3 h time-on-stream, this In-based catalyst was observed to lose 6% propene yield over a total of 12 h on stream. Considering that deactivation is the most significant issue plaguing the use of N<sub>2</sub>O as an oxidant in the ODH-N<sub>2</sub>O reaction of propane, the In<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> has good potential to be an active and stable catalyst.

In summary, although Fe-ZSM-5 has the most potential for the ODH-N<sub>2</sub>O reaction for propane, several other catalysts have been tested. Vanadia based catalysts have been shown to be highly active for the reaction, which were found to be more selective when supported on less acidic, silica-based support materials, and at loading levels of lower than 5 wt%. Indium based catalysts have also been suggested for the ODH-N<sub>2</sub>O reaction, with the potential for a highly stable catalyst compared to Fe-ZSM-5, which displays significant deactivation and is likely to be the underlying reason behind the relatively low research effort put into the N<sub>2</sub>O route compared to the other potential oxidants described in this review article.

## 8. Summary of propane dehydrogenation and over-arching themes in catalyst design

In the above sections, the literature on the catalytic dehydrogenation of propane has been critically reviewed. Each sub-reaction of propane dehydrogenation has specific kinetic and



thermodynamic requirements, and this is reflected in the diverse variety of catalysts that have been developed in recent decades. Throughout this review we have attempted to compare the productivity of catalysts for DDH and the various ODH reactions by measuring space time yield of the catalyst (*i.e.*, the moles of propene produced per kg of catalyst per hour). This is an imperfect metric with which to compare catalysts, but the wide range of reaction conditions and catalyst types explored means that calculating turnover frequencies for each catalyst is not possible. One assumption when comparing productivity is that catalysts are tested under conditions to maximise their performance. This is of course not the case for all studies, especially those where kinetic measurements were of interest, or where there were other constraints present. However, by comparing the range of values associated with a single class of catalyst, it is possible to identify the highest performing catalysts in each class and broadly assess the potential of each. Fig. 11 below compares a selection of literature catalysts (presented in Tables 2–14) for each reaction, colour-coded to highlight the performance of different elements in different reactions. The horizontal dashed line is marked at the equivalent of  $5 \text{ kg}_{\text{C}_3\text{H}_6} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$ , which has been considered to be space time yield that may warrant consideration of commercial application.<sup>196,213</sup> Such a value is difficult to pinpoint, but given that this is where the more active Pt and  $\text{CrO}_x$  catalysts for DDH are found, it is reasonable.

It is clear that for the DDH reaction, Pt- and Cr-based catalysts dominate the highest space time yield measurements. This is expected given their widespread use in industrial processes. Beyond this,  $\text{ZrO}_2$  and  $\text{ZnO/ZrO}_2$  catalysts perform strongly, and their low cost and low toxicity make them well-suited for commercial application. These materials have only recently been reported in the literature and with further devel-

opment they may match or outperform Pt- and Cr-based catalysts. It is also possible that they are already present in the K-PRO process.

In  $\text{ODH-O}_2$ , B-based catalysts are the best performing, with STY values in excess of  $70 \text{ mol}_{\text{C}_3\text{H}_6} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$  reported. Some boron catalysts exceeded  $200 \text{ mol}_{\text{C}_3\text{H}_6} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$ , well above the  $5 \text{ kg}_{\text{C}_3\text{H}_6} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$  threshold and underscores their potential for commercial application. Although  $\text{ODH-O}_2$  produces  $\text{H}_2\text{O}$  as a side-product (rather than  $\text{H}_2$ ), ethene is typically the major by-product in B-catalysed reactions rather than coke formation. As an exothermic reaction, large-scale implementation may be preferable to the endothermic DDH reaction, which requires specific heat-generating technology to be efficient. Therefore the commercialisation of a  $\text{ODH-O}_2$  process using B catalysts may be realistic.

$\text{ODH-CO}_2$  catalysts do not yield more than *ca.*  $20 \text{ mol}_{\text{C}_3\text{H}_6} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$ , which suggests that  $\text{CO}_2$  activation remains a key challenge. While  $\text{CrO}_x$  based catalysts yield the highest STY, only incremental advances have been made in recent years and it will take a step-change in catalyst development before  $\text{ODH-CO}_2$  can be meaningfully compared to DDH and  $\text{ODH-O}_2$  reactions, as a mean to produce propene. Interestingly, some of the highest STY values reported are  $\text{CrO}_x/\text{activated carbon}$  and  $\text{FeO}_x/\text{activated carbon}$ . The obvious drawback of activated carbon as a support is that oxidative regenerations will combust the support, but clearly its chemical properties are desirable as a catalyst support.

In  $\text{ODH-N}_2\text{O}$ , Fe-ZSM-5 are the most active catalysts known, and in one example a STY of  $178 \text{ mol}_{\text{C}_3\text{H}_6} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$  was reported.  $\text{ODH-N}_2\text{O}$  is the least studied sub-reaction and it is thought that the relatively high cost and low availability of  $\text{N}_2\text{O}$  may be the most limiting aspect.  $\text{N}_2\text{O}$  is a by-product in various chemical processes including adipic acid and nitric

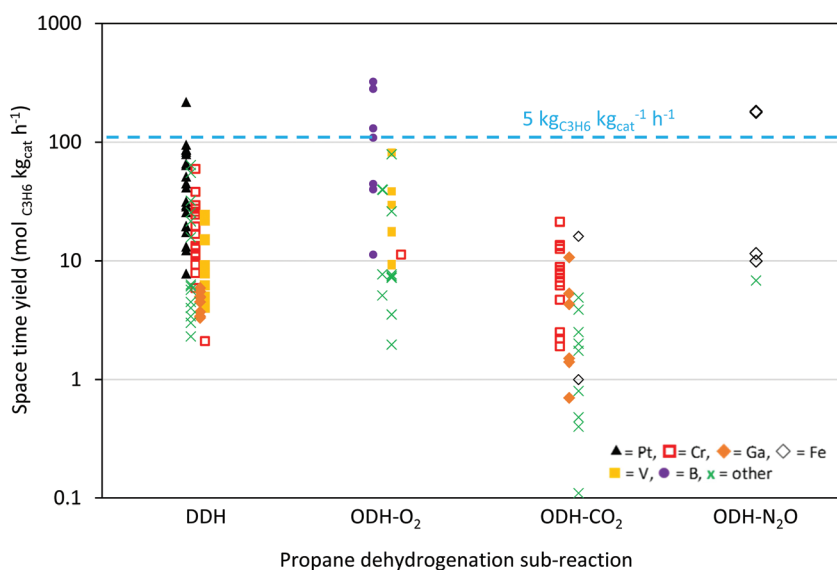


Fig. 11 Space time yield plot of a selection of DDH,  $\text{ODH-CO}_2$  and  $\text{ODH-O}_2$  catalysts, showing the relative performance of catalysts in each sub-reaction.



**Table 16** Summary of reaction conditions and catalyst properties in each dehydrogenation sub-reaction

Reaction	Reaction temperature range /°C	Significant side reactions	Role of redox sites	Role of acid sites	Role of basic sites	Typical deactivation mechanisms
DDH	550–630	Coking, cracking	Not directly involved	Alkane activation, strong acid sites promote coking	Alkene desorption	Coking
ODH-CO <sub>2</sub>	400–600	Dry reforming, coking, cracking	CO <sub>2</sub> activation	Alkane activation, strong acid sites promote coking	Alkene desorption, CO <sub>2</sub> activation	Coking, overreduction of catalyst
ODH-O <sub>2</sub>	400–600	Overoxidation, cracking	O <sub>2</sub> activation	Alkane activation	Alkene desorption	Sintering
ODH-N <sub>2</sub> O	400–600	Overoxidation, coking, cracking,	N <sub>2</sub> O activation	Alkane activation, strong acid sites promote coking	Alkene desorption	Coking

acid production, but there may be few other opportunities for large-scale sequestration and utilisation of N<sub>2</sub>O on an industrial scale. It is also apparent that the selectivity to propene is often below 70% and the catalysts rapidly deactivate on-stream.

Table 16 below shows a summary of the typical chemical and catalytic properties associated with each reaction. While the temperature range of each reaction overlaps, generally ODH-O<sub>2</sub> and ODH-N<sub>2</sub>O are carried out at lower temperature than DDH, while ODH-CO<sub>2</sub> typically lies in between or nearer to DDH reaction temperatures. In terms of side-reactions, cracking is the only common source of by-products in each sub-reaction. Coking remains a major challenge in DDH, ODH-CO<sub>2</sub> and ODH-N<sub>2</sub>O, while overoxidation is generally observed in the ODH-O<sub>2</sub> and ODH-N<sub>2</sub>O processes. Redox sites play an active role in each of the oxidative dehydrogenation reactions, while in DDH they are not required. The importance of acid and base sites have been frequently examined across each sub-reaction, and interestingly remain the only catalytic properties that are applicable to each sub-reaction. Acid sites are widely known to activate alkanes, but if the acid sites are too strong, the alkane will be retained on the surface and lead to coking, or overoxidation in the case of ODH-N<sub>2</sub>O and ODH-O<sub>2</sub> reactions. Basic sites on the other hand, are known to facilitate alkene desorption and in the case of ODH-CO<sub>2</sub>, to activate CO<sub>2</sub>. Therefore, a balance of these sites is necessary to promote sufficient propane activation and propene desorption. Prevalent deactivation mechanisms also vary between sub-reactions, with coking frequently cited as a cause for loss of on-stream activity in DDH, ODH-CO<sub>2</sub> and ODH-N<sub>2</sub>O. The ODH-O<sub>2</sub> catalysts on the other hand are generally much more stable on-stream. It is noteworthy however, that despite relatively fast deactivation of DDH catalysts, the activity can be regenerated after an oxidative treatment, significantly extending the catalyst lifetime.

Regarding catalyst design for each reaction, there are catalysts that can efficiently operate for DDH, ODH-CO<sub>2</sub> and ODH-O<sub>2</sub>, while there are some that are reaction-specific. This is exemplified by supported chromium oxides, which have been reported for DDH, ODH-CO<sub>2</sub> and ODH-O<sub>2</sub>. On the other hand, Fe-ZSM-5, which is highly active for ODH-N<sub>2</sub>O has a

unique dimeric Fe<sup>2+</sup> site that can activate N<sub>2</sub>O but not O<sub>2</sub>. Therefore, it would not be applicable to ODH-O<sub>2</sub> or DDH. The ability of Cr to catalyse multiple sub-reactions is likely to be related to its stability (and activity) in multiple valence states. In DDH, Cr<sup>3+</sup> sites are considered the active species, while in ODH-CO<sub>2</sub> and ODH-O<sub>2</sub>, the redox cycle of Cr to Cr<sup>4+</sup> and Cr<sup>3+</sup> all facilitate the activation of the oxidant. Supported vanadia catalysts can also exhibit multiple valence states, and are also active in DDH, ODH-CO<sub>2</sub> and ODH-O<sub>2</sub>.

Aside from the active element, catalyst supports also comprise a vital component of any propane dehydrogenation catalyst. The primary role of the support is to enhance and maintain high dispersion of the active phase. This has been demonstrated multiple times over metal oxides such as those of Ga, Cr, V and Fe, where SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub> have been widely implemented as supports. The acid and base sites of the support also affect the performance of the catalyst and can be adjusted with promoters. This strategy has been widely applied in DDH catalysts. The support may also play a more active role in catalysis, by activating propane, CO<sub>2</sub> or O<sub>2</sub>.

A multitude of chemical elements including precious metals, rare earth metals, base metals and non-metals have all been discovered to play a role in catalysing propane dehydrogenation in various contexts. Any sustainable process should aim to use abundant and renewable raw materials, and this applies to the catalyst as well as the starting reactants. It is clear that across the more active propane dehydrogenation catalysts known, there is a range in the abundance and production of the chemical elements required. Table 17 summarises the availability of a range of chemical elements commonly applied in propane dehydrogenation catalysts.

In the DDH reaction, the most active elements are typically Pt and Cr, which are already implemented in commercial processes, and more recently Zr and Zn-based alternatives have been used. While chromium is relatively abundant as a chemical element, Pt is very scarce and production limited to a few countries, namely South Africa. The global reserves of individual platinum group metals (PGMs) is not possible to accurately quantify, but it is estimated that the total global reserve of PGMs is over 100 000 tonnes meaning that Pt and Pd are easily





**Table 17** Global production and abundance of chemical elements typically employed in propane dehydrogenation catalysts

Chemical element	Common mineral form	Annual production in 2019/10 <sup>3</sup> tonnes	Estimated world reserves/10 <sup>3</sup> tonnes
Boron	B <sub>2</sub> O <sub>3</sub> , other borates	>3500	>1 200 000
Chromium	chromite	44 000	570 000
Gallium	Trace element in other minerals (<50 ppm)	0.44 <sup>a</sup>	560 <sup>a</sup>
Palladium	Metallic	0.21	Unknown
Platinum	Metallic	0.18	Unknown
Vanadium	Oxidic form	73	>63 000
Zinc	Sphalerite	13 000	1 900 000
Zirconium	ZrSiO <sub>4</sub>	1400	64 000

<sup>a</sup> From ref. 317 which uses data for 2014. Unless otherwise stated, the values were reproduced from ref. 318.

the most scarce chemical elements commonly used for propane dehydrogenation. While supported nanoparticle catalysts use a fraction of the quantity of metal that would be required in a metal oxide catalyst, it would be desirable for any DDH process to use an abundant, non-toxic element as the main component of the catalyst. This makes the recent discovery of Zr/TiZnO<sub>x</sub> all the more promising.<sup>157</sup> The ODH-O<sub>2</sub> reaction has recently been dominated by the discovery of boron-based catalysts, which are highly abundant compared to most other ODH-O<sub>2</sub> catalysts such as V. Accordingly it should be considered a good candidate for commercialisation from the point of view of sustainability. ODH-CO<sub>2</sub> catalysts are typically Cr or Ga based. As described above, Cr is highly abundant but also toxic. Gallium is present in the Earth's crust at around 17 ppm (ref. 319) and is typically found as an impurity in minerals such as bauxite, sphalerite and germanite. Although present as a trace element in these minerals, the abundance of bauxite is vast and it is estimated that the amount of gallium contained in bauxite alone is 560 000 tonnes, which places it well above platinum in abundance. The field of research into DDH and ODH-O<sub>2</sub> is very diverse, and in recent years a number of novel discoveries has expanded the range of catalytically active elements known for this reaction. This means that the reliance on scarce elements like Pt, or toxic ones like Cr is limited. Future sustainable DDH and ODH-O<sub>2</sub> processes should capitalise on this knowledge and implement abundant elements such as B, Zn, V or Zr. With regards to ODH-CO<sub>2</sub>, the performance of the most active catalysts is still well below what would be considered for commercialisation, but the research community should look to the successes of the above-mentioned abundant elements for inspiration in designing novel ODH-CO<sub>2</sub> catalysts.

## 9. Outlook

While the current focus of government policy is based on net zero carbon, it is clear that society will still need a wide range of products based on carbon-containing molecules. It is now essential that the chemical industry focusses on accessing such carbon from sustainable sources. It is likely that for the near- and mid-range future the current key platform molecules such as propene will still be required. Against this background,

the dehydrogenation of propane will remain a major industrial process and its future importance is guaranteed due to the scale and breadth of propene applications in modern society. Currently, the majority of propane is sourced from non-renewable feedstocks, but the industry has recognised the need to change and steps have been taken to develop processes for renewable propane to be generated. It may be many years before so-called bio-propane can compete with non-renewable propane sources in terms of supply, but the catalytic processes described in this review will be required to enable this technology to be used. Therefore, the development of catalysts for the direct dehydrogenation of propane in the presence or absence of an oxidant will continue to attract attention from academia and industry alike, as significant advances have been made in recent years. An analysis of the sustainability of current C<sub>3</sub>H<sub>6</sub> production methods, namely steam cracking and methanol-to-olefins, reveals that direct dehydrogenation has several advantages in efficiency when a selective catalyst is applied. Life cycle analyses of oxidative dehydrogenation reactions using O<sub>2</sub> and CO<sub>2</sub> have not been carried out, due to the fact that these reactions have not been commercialised yet. However, in principle the processes have the potential to offer lower temperature routes to forming C<sub>3</sub>H<sub>6</sub> without lengthy catalyst regeneration steps.

DDH is to date the only reaction that has been operated commercially. The most active catalysts reported in the literature are based on chromium oxide or platinum promoted with tin oxide, but even these require frequent regeneration due to coking. Therefore, the future of DDH catalyst design should focus on reducing deep dehydrogenation reactions that lead to coking. Irrespective of catalyst, common themes have been established in efforts to improve C-H bond activation, reducing propane and hydrogen adsorption on surface sites. Of these, supports with weak and moderate surface acidity coupled promoting elements (B, Ga, Cu and Ni to name a few) result in lower Pt utilisation, which is desirable for potentially industrially applicable catalysts. Additionally, a number of noble, non-noble based intermetallic alloys and numerous mixed metal oxides are emerging as viable alternatives to chromium oxide or platinum-based catalysts; and this presents an economic and environmental benefit. In doing so, the frequency of regeneration will be reduced, meaning that fewer CO<sub>2</sub> forming regeneration cycles will be required, thus reducing the carbon footprint of propane production.



ODH-O<sub>2</sub> offers a pathway that avoids the formation of coke entirely, but until recently, the STY typically reported in ODH-O<sub>2</sub> catalysts such as supported vanadia were, with few exceptions, an order of magnitude below that of DDH catalysts. The advent of boron-based catalysts for this reaction has led to a significant increase in the prospects for commercial application. As a relatively stable, non-hazardous and abundant element, boron catalysts may well play a major role in future propene production processes. Furthermore, they appear to be stable on-stream in laboratory tests, although industrially relevant stability tests have not yet been reported.

ODH-CO<sub>2</sub> has attracted interest, mostly in academia,<sup>320</sup> due to the prospect of utilising CO<sub>2</sub> and developing carbon neutral or carbon-negative processes. This is determined by the downstream use of CO, the primary product of CO<sub>2</sub> dissociation. Although ODH-CO<sub>2</sub> catalysts are not known to overoxidise propane, the drawbacks associated with DDH, *i.e.*, coking, often remain and the inertness of CO<sub>2</sub> means that low STYs are frequently reported. The majority of investigations thus far have focussed on Ga- or Cr-based catalysts and improvement in these catalysts has been incremental. Supported nanoparticles on the other hand, have received little attention despite showing some promising results. In this class of catalysts, minimising competing reactions such as reforming, is essential. Future catalyst design should aim to move away from Cr- and Ga-based catalysts to focus on low-temperature CO<sub>2</sub> activation and have controlled redox and acid-base properties. For this reaction to become significant beyond academic interest, a step-change in catalyst performance is needed.

ODH-N<sub>2</sub>O is the least studied reaction and progress has not been substantial in recent years. This may be due to the unfavourable economic costs associated with using N<sub>2</sub>O as an oxidant, although in an integrated facility where N<sub>2</sub>O is produced as a by-product this could be a useful approach. In terms of catalyst performance, the most active catalyst, Fe-ZSM-5, can achieve a similar STY to the more active DDH and ODH-O<sub>2</sub> catalysts. However, the intrinsic selectivity to propene is often below 70% and is undoubtedly the main disadvantage. If propene selectivity can be improved to 90%+, the catalyst would out-perform some of the most active DDH and ODH-O<sub>2</sub> catalysts reported in the literature.

## Conflicts of interest

There are no conflicts to declare.

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