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Review

# Oxidative dehydrogenation of propane to propylene with carbon dioxide

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ABSTRACT

Oxidative dehydrogenation of propane in the presence of carbon dioxide (ODPC) is a sustainable approach and an attractive catalytic route for propylene production with less environmental footprint than the conventional oxidative dehydrogenation path with oxygen. Researchers have considered $CO_2$ as a mild oxidant that can overcome the problems of over-oxidation and low propylene selectivity, that are typically associated with the current synthesis routes. This article provides a critical review on the current mechanistic understanding of three different catalyst types used in the ODPC reaction based on experimental studies; (i) zeolites with different frameworks, (ii) porous materials-supported metal oxides, and (iii) transition metal oxides and other metal catalysts. A detailed review of the literature compares the framework, pore structure, nature of active sites, reducibility, and the role of promoters and supports for each type of catalytic materials in the absence and presence of $CO_2$, and is followed by a thorough discussion on the promotional effects of $CO_2$ as a soft oxidant on C—H bond scission. Future directions with respect to materials design, synthesis and reaction conditions are also discussed.

## 1. Introduction and motivation

Selective dehydrogenation of propane to propylene is one of the major challenges for production of valuable and versatile chemical feedstocks. The current industrial on-purpose propylene production through dehydrogenation of ethane and propane is non-oxidative in nature and is contributing to quick catalyst deactivation, low conversion and selectivity, and high reaction temperatures [1]. The current state-of-the-art research has primary focused on investigating the synergistic effects between gas phase oxidants and alkanes in order to overcome the hindrances in current industrial dehydrogenation reactions [2–5]. It is established that catalytic oxidative dehydrogenation (ODH) reactions are sensitive to specific oxidants [6,7]. A number of oxidants such as oxygen [6,8], nitrous oxide [6,9] and carbon dioxide [10,11] have been considered as co-feed in propane dehydrogenation reactions. Although, oxidative dehydrogenation of propane (ODP) in the presence of molecular $O_2$, as an oxidizing agent, favors low temperature reactions and is exothermic with no thermodynamic limitations [12,13], deep oxidation of propane and propylene to $CO_x$ is a major drawback, which often results in loss of propylene selectivity and yield [13–15]. To address these issues, an alternative approach has been proposed by which $O_2$ is replaced with a milder oxidant such as $CO_2$ to convert propane to propylene over various heterogeneous catalysts.

Most experts studying the global ecosystem and climate suggest that rising anthropogenic $CO_2$ emissions have contributed to significant global climate change in the last half-century [16–21]. The development of effective strategies that convert such $CO_2$ emissions into energy, fuels, and chemicals are greatly preferable to oceanic or geologic sequestration options because they offer the potential to create new commercially-viable products from renewable carbon feedstock in a sustainable manner [2,22–24]. However, $CO_2$ is a thermodynamically stable molecule ($\Delta G_f = -394\ \text{kJ mol}^{-1}$) with a high oxidation state, hence, reactions of $CO_2$ must be combined with a high-energy reactant, effective catalysts and reaction conditions to gain a thermodynamic driving force [24,25].

The objective of this paper is to provide a critical review of the state-of-the-art materials that have been investigated for catalyzing the ODP reaction with $CO_2$ (ODPC) in order to establish a useful guideline for extrapolating and normalizing the reported ODPC reaction data to identify correlations between catalyst properties and performance. Among heterogeneous catalysts studied for the ODPC reaction so far, zeolites with the MFI and CHA frameworks, chromium- [26,27], platinum- [28,29], vanadium- [6,30] and gallium-based catalysts [31,32] are found to be the most efficient materials mainly due to their high activity and easy regeneration [33,34]. Literature shows that the catalytic activity of these materials depends upon various factors including the nature of support [10], promoters [35], and the synthesis

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procedures [36,37]. Therefore, in this review, we will focus on reviewing the effects of $CO_2$ partial pressure, acid-based properties and porosity of different zeolites, metal oxides reducibility and bifunctional catalysts (*i.e.*, metal-supported zeolites) on the conversion of propane, selectivity of propylene, and the kinetics of the ODPC reaction. In addition, the effect of process conditions on the ODPC reaction is discussed and future research directions are provided.

## 2. Oxidative dehydrogenation of propane with $O_2$ and $CO_2$

Despite the extra ordinary effect of molecular $O_2$ (exothermicity and equilibrium support effect), deep oxidation of products has been confirmed even at small doses of $O_2$, resulting in reduced selectivity to propylene. Aside from this deep oxidation, the high exothermicity of $O_2$ generates great amount of energy that must be removed [1,13,31]. In general, the major drawback of ODP with $O_2$ is that the propylene yield is typically low on a laboratory scale, as stated above, and that the role of catalysts and their fast deactivation in the presence of $O_2$ are not well-understood [12,13,38]. For instance, by reviewing the literature in the period of 1995–2017, the best propylene yield of 40% has been reported for ODP with $O_2$ which is still far from industrial implementation and the information concerning the catalyst lifetime appeares quite limited [1,13,27,39–42]. The scale-up of catalytic materials and/or reactor configurations capable of maintaining high selectivity to propylene under conditions leading to high propane conversion is another aspect that has been often overlooked.

A comprehensive review of the literature on the dehydrogenation of light alkanes that covers exclusively metal and metal-oxide catalysts has been undertaken by Sattler et al. [1]. Their review provided a summary of parameters including nature of active sites, type of supports and promoters, and feed composition, affecting the catalytic properties and lifetime of systems based on $GaO_x$, $VO_x$, $MoO_x$, Pt and Pt-Sn, and $CrO_x$ supported catalysts [1]. In other reviews, Pt-based catalysts have been discussed from the perspective of catalyst design [43], mass transfer limitations, and the influence of hydrogen combustion on olefin yield [44]. Albonetti et al. [45] discussed the chemistry of vanadium in ODP reaction in their review. Cavani et al. [38] compiled a review on over 100 catalysts with different active phases for the ODP reaction with $O_2$ as a co-feed. In that review, features of catalysts with remarkable performance, reaction network of partial and total oxidation, and the influence of homogenous gas phase reactions on the formation of olefins in ODH of alkanes were covered [38]. Recently, Carrero et al. [13] reviewed the kinetics of ODP over $VO_x$ catalysts with the focus on the effects of catalyst synthesis method, molecular structure of supported vanadium oxide species, reaction mechanism, and structure-activity relationship of the vanadium-based catalysts.

Several other reviews exist on the ODH of alkanes with $CO_2$. For instance, Krylov et al. [46] reviewed the oxidation of hydrocarbons and alcohols with $CO_2$ over manganese oxide catalysts in 1995. The authors concluded that manganese oxide-based catalysts are active, selective, and do not form a carbon layer during the reaction in dry reforming of methane and oxidative dehydrogenation of $C_2$–$C_7$ hydrocarbons and the lower alcohols. Another mini-review by Wang et al. [40] discussed dry reforming of methane and dehydrogenation of light alkanes in the presence of $CO_2$, more than a decade and half ago. The information in that review was limited to $CH_4$, with no in-depth discussion on $C_2H_6$ and $C_3H_8$ conversion and no consideration of microporous materials such as zeolites [40]. Other notable reviews on the use of $CO_2$ as a mild oxidant for the dehydrogenation of alkanes, especially ethylbenzene and methane in the presence of $CO_2$ have been provided by Ansari and Park [2] and Kawi et al. [24].

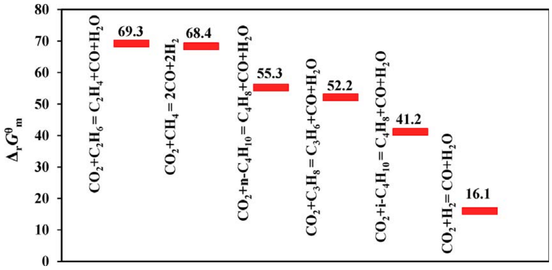

**Fig. 1.** $\Delta_r G^\theta_m$ of the reactions between $CO_2$ and light alkanes at 400 °C and normal pressure [5,25].

## 3. Thermodynamic analysis of dehydrogenation of light alkanes with $CO_2$

Recently, the use of $CO_2$ in oxidative dehydrognation of light alkanes has received significant attention as it has been shown to shift the ODH reaction toward more olefin production compared to molecular $O_2$ by preventing deep oxidation of the reaction products and as a coke removal agent from the catalyst [47,48]. As shown in Fig. 1, the Gibbs free energy changes of $CO_2$ ($\Delta_r G^\theta_m$) reaction becomes increasingly favorable by moving towards higher alkanes.

Recently, Edwards et al. [25] investigated the effect of temperature and $CO_2$ on the Gibbs free energy for dehydrogenation of light alkanes from 300 to 500 °C and reported that although all ODH reactions of light alkanes with $CO_2$ show a similar trend, ethane dehydrogenation displays the highest $\Delta_r G^\theta_m$ (Fig. 1), indicating that it is much harder to operate this reaction as compared to propane and butane dehydrogenation reactions at 300–500 °C. Furthermore, the dehydrogenation of propane with $CO_2$ was more favorable than *n*-butane but less feasible than *i*-butane, as shown in Fig. 2. The butane has multiple curves because of its constituent isomers. Therefore, $\Delta_r G^\theta_m$ does not keep falling as the carbon number of alkane increases and lower value of $\Delta_r G^\theta_m$ indicates a higher possibility of cracking. The authors also studied the $\Delta_r G^\theta_m$ of light alkanes and olefins cracking to generate carbon and $H_2$ and found that (i) olefins show a much higher cracking possibility than alkanes, (ii) propylene has a much higher resistance to cracking than any isomers of butane, (ii) the selectivity of the target products is significantly affected by further cracking of the olefin. As can be seen from Fig. 3a, although ethylene has higher resistance to subsequent cracking compared to propylene, it is more difficult for ethane to be activated with $CO_2$ when the temperature is kept below 500 °C (Fig. 3a). Therefore, from thermodynamics perspective, the ODPC is the best dehydrogenation pathway below 500 °C in comparison to other alkanes.

In general, alkanes dehydrogenation reactions with $CO_2$ are very complicated because they are thermodynamically limited at low

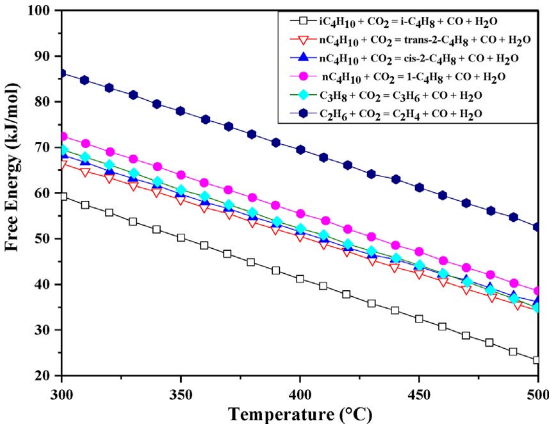

**Fig. 2.** $\Delta_r G^\theta_m$ of the ODH of light alkanes in the presence of $CO_2$ at 300–500 °C [25].