



Thermodynamic equilibrium analysis on oxidative dehydrogenation of propane using CO₂: Finding a suitable reactant ratio for propylene formation

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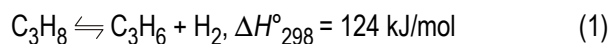
Thermodynamic equilibrium analysis has been employed to propose a suitable reactant ratio for propylene formation from oxidative dehydrogenation of propane reaction. The reactants and products were modelled in RGibbs reactor to understand the effect of temperature, addition of carbon dioxide and inert molecules on top of equimolar feed between propane and CO₂. The desired product propylene is formed along with other undesired products like CO over a broad range of temperature. The formation of propylene is significantly affected by CO forming side reactions such as reverse water gas shift and dry reforming of propane which are endothermic in nature. The reactant stream with equimolar CO₂ and propane appears to be the most favourable for propylene formation. The higher operating temperature should be avoided to minimize CO and maximize propylene formation.

Keywords: CO₂, propane, oxidative dehydrogenation, propylene, reactant ratio.

Introduction

The existing non-oxidative dehydrogenation processes for propylene production include fluidized catalytic, thermal and hydrocracking of propane which have several limitations including a high capital investment, additional down streaming and low selectivity to propylene owing to the dominance of side reactions¹.

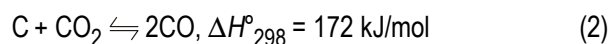
The direct dehydrogenation of propane (DDP) is endothermic, hence higher



operating temperature is required, leading to an increased coke formation. Excessive coke can block the active sites of the catalysts and decrease its lifetime, adding frequent catalyst regeneration to operation costs. High operating temperatures also put a thermodynamic limitation on the equilibrium conversion^{2,3}. Earlier, oxidative dehydrogenation of propane (ODHP) using O₂ to propylene has been studied in great detail⁴⁻⁷. A greater challenge of over-oxidation is put forth when using O₂ for this reaction. Over oxidation of propane may favor the formation of carbon oxides and hence reduce

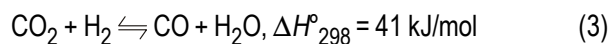
propylene selectivity. Moreover, secondary problems pertaining to the flammability of the reaction mixture, necessary removal of excessive energy and the possibility of a runaway reaction limit the practical application of this reaction^{1,3,6,8}. This led to the use of CO₂ as a mild oxidant for ODHP by replacing O₂. This viable alternative became a promising area of research for the benefits of (i) prevents over-oxidation, (ii) contributes significantly in reducing the environmental footprint of CO₂ and (iii) production of propylene being an essential building block in chemical industry, thus having an avenue for CO₂ valorization to value-added products⁹⁻¹¹.

Interestingly, the CO₂ present in ODHP may act as a coke removing agent, which occurs due to propane dehydrogenation over the catalyst site, indirectly contributing to the increase in catalyst lifetime, as represented by the reverse Boudouard reaction.



The reaction is highly endothermic and thus at low temperature favoring the formation of CO₂. However, as the temperature increases, the free energy of CO₂ remains insensi-

tive to temperature change, making the overall reaction more favorable to CO formation^{12,13}. It was also observed that the use of CO₂ favored propylene selectivity owing to one or both of the pathways: (i) reverse water gas shift pathway (RWGS),



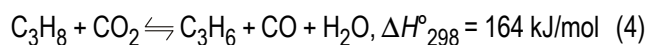
according to which CO₂ consumes H₂ produced during DDP to give CO and H₂O, thus shifting the reaction to the forward direction and letting off the thermodynamic limitations, and (ii) MvK (Mars van Krevelen) pathway, according to which CO₂ promotes the dehydrogenation by re-oxidizing the catalyst surface sites which was reduced by propane to form propylene^{1,3,8,14}.

Current attention has been focused on the suitability of implementing oxidative dehydrogenation of light alkene (propane), due to its selectivity towards olefin (propylene) production^{1,3,5,6,15,16}. Previous studies showed that the Gibbs free-energy changes of ODH of alkane become more negative with higher alkanes ($i\text{-C}_4 > \text{C}_3 > n\text{-C}_4 > \text{C}_2$)¹⁷⁻¹⁹.

ODHP using CO₂ is characterized by rapid catalyst deactivation due to coke formation^{1,6,15,19}. Therefore it is extremely important to examine the effect of operating conditions on the propylene formation before any catalyst formulation begins. The combination of reactions (1-3) could be favored according to the catalyst formulation and operating conditions chosen. Therefore, different sets of equilibrium could be approached. Thermodynamic equilibrium analysis on combination of reactions incorporating the possible products from known set of reactants is an important step in the design of suitable catalyst²⁰. It actually provides a basis for experimental and computational studies, as well as understanding the boundaries and constraints that thermodynamics imposes on process and catalyst development³. The thermodynamics of ODHP using CO₂ has been studied earlier^{1,3} however, the effect of reactant ratio in the light of excess CO₂ and temperature on the desirable product propylene is scarce. It is the very purpose of this study to provide results of the effect of increasing CO₂ partial pressure, temperature and inert addition to the propylene formation.

In the present study the reactants and products considered were CO₂, C₃H₈ and C₃H₆, CO, H₂, H₂O respectively. These components represent the combination of reaction (1) and (3) making it a two step ODHP. Moreover, absence of any side reactions such as RWGS and reverse Boudouard

were ensured and single step ODHP was studied to compare the



conversion and formation of propylene with regard to two step ODHP. Finally, the effect of inert N₂ was observed on the propane conversion and propylene formation by adding to equimolar C₃H₈ and CO₂ feed.

Methods:

Thermodynamic equilibrium analysis of ODHP using CO₂ was performed using AspenPlus V8.8 software. It was previously used for oxidative dehydrogenation of ethane²¹. Equilibrium conversion of propane, $X_{\text{eq,C}_3\text{H}_8}$ (%), and propylene formation, $\text{neq}_{\text{C}_3\text{H}_6}$, were determined by using RGibbs reactor. This reactor model employs Gibbs free energy minimization algorithm subject to atom balance constraints. The feed containing C₃H₈ and CO₂ ratio was varied from equimolar to 1:4 ratios. The temperature was also varied from 600–1300 K on all the simulation runs under a constant pressure at 1 bar. Moreover, to distinguish the role played by CO₂ on the propane conversion and propylene formation in ODHP, a separate simulation run for DDP was considered. Here, inert nitrogen was introduced to keep the propane partial pressure similar for meaningful comparison between DDP and ODHP. Finally, the effect of inert N₂ in ODHP was carried out by varying the feed ratio as 1:1:1, 1:1:2 and 1:1:3. However, in order to begin with calculation without complication, any aspects of fluid dynamics, heat transfer limitations in the reactor and side reactions leading to carbon formation and catalyst deactivation are not taken into consideration.

Results and discussion

The equilibrium conversion, $X_{\text{eq,C}_3\text{H}_8}$ (%), of propane for single and two step ODHP was calculated at 820 K and 1 bar total pressure and compared in Table 1. It is observed that two step ODHP increased $X_{\text{eq,C}_3\text{H}_8}$ over single step for all partial pressure of propane considered. This suggests that H₂ formed by DDP is used in the RWGS reaction which effectively moves the equilibrium towards right and enhanced the propane conversion. Similarly, Table 2 reported the equilibrium formation of propylene ($\text{neq}_{\text{C}_3\text{H}_6}$) using the same temperature and pressure and it was observed that when CO₂ was present in excess to equimolar amount, the formation of propylene was not favoured. With increase in CO₂ partial pressure, the formation of propylene was decreased. Over-

Table 1. Equilibrium conversion of propane at T = 820 K, P = 1 bar for ODHP reaction

$P_{C_3H_8}$ (bar)	Xeq _{C₃H₈} (%) single step ODHP		Xeq _{C₃H₈} (%) two step ODHP	
	(C ₃ H ₈ :CO ₂)	(C ₃ H ₈ :CO ₂ :N ₂)	(C ₃ H ₈ :CO ₂)	(C ₃ H ₈ :CO ₂ :N ₂)
0.50	13.2 (1:1)	–	46.0 (1:1)	–
0.33	22.9 (1:2)	13.9 (1:1:1)	69.3 (1:2)	48.7 (1:1:1)
0.25	32.0 (1:3)	14.3 (1:1:2)	90.3 (1:3)	51.0 (1:1:2)
0.20	40.9 (1:4)	14.7 (1:1:3)	99.5 (1:4)	53.0 (1:1:3)

Table 2. Equilibrium formation of propylene at T = 820 K, P = 1 bar for ODHP reaction

$P_{C_3H_8}$ (bar)	neq _{C₃H₆} (kmol) single step ODHP		neq _{C₃H₆} (kmol) two step ODHP	
	(C ₃ H ₈ :CO ₂)	(C ₃ H ₈ :CO ₂ :N ₂)	(C ₃ H ₈ :CO ₂)	(C ₃ H ₈ :CO ₂ :N ₂)
0.50	0.026 (1:1)	–	0.141 (1:1)	–
0.33	0.025 (1:2)	0.027 (1:1:1)	0.075 (1:2)	0.16 (1:1:1)
0.25	0.024 (1:3)	0.028 (1:1:2)	0.023 (1:3)	0.18 (1:1:2)
0.20	0.022 (1:4)	0.029 (1:1:3)	0.001 (1:4)	0.20 (1:1:3)

all, two step ODHP was advantageous than single step with regard to propylene formation except when CO₂ was present in 1:4 (C₃H₈:CO₂) molar ratio.

The Xeq_{C₃H₈} and neq_{C₃H₆} were calculated for different reactant ratio and are shown in Fig. 1 for DDP and in Fig. 2 for ODHP. The partial pressure of propane was kept the same while analyzing thermodynamic equilibrium on DDP and ODHP in order to draw meaningful comparison. A comparative analysis between Figs. 1 and 2 indicated that introduction of CO₂ in ODHP improved the equilibrium C₃H₈ conversion and more specifically, beyond the equimolar ratio between C₃H₈ and CO₂, the temperature needed for achieving a particular C₃H₈ conversion was lowered. This suggests that other side reactions i.e. RWGS and propane reforming with CO₂ possibly occurred which effectively increased C₃H₈ conversion by shifting the equilibrium towards right.

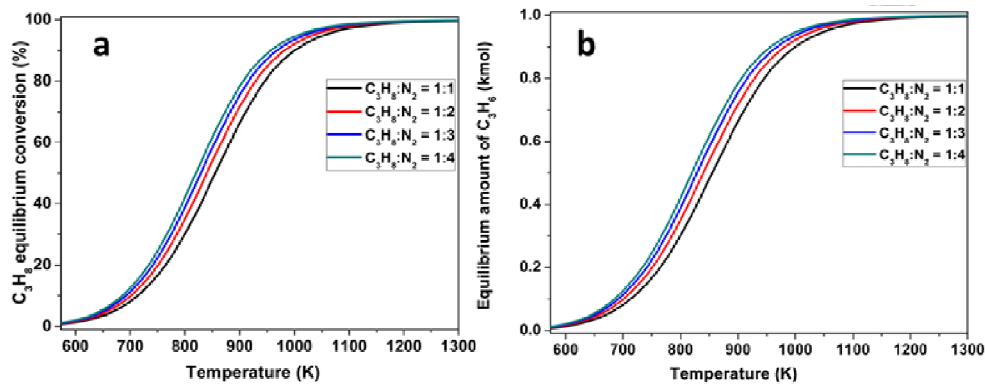


Fig. 1. (a) Equilibrium percentage conversion of propane, (b) equilibrium amount of propylene as a function of temperature and the ratio of reactant gases for DDP reaction.

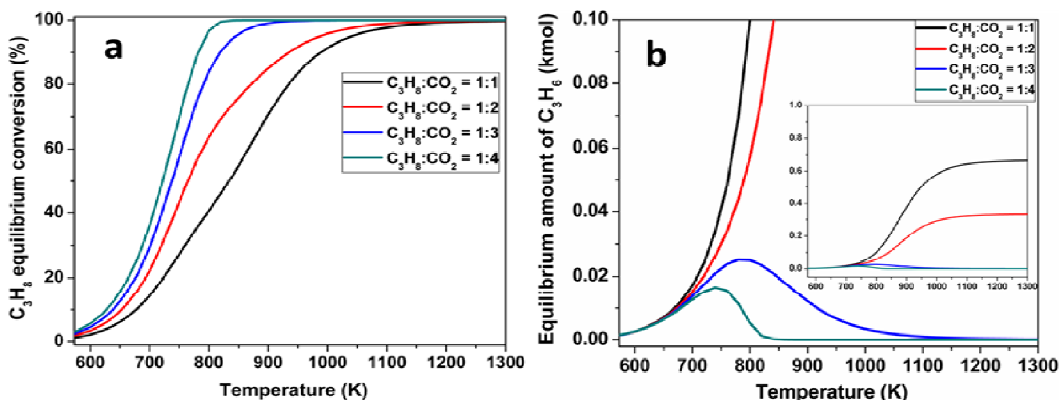
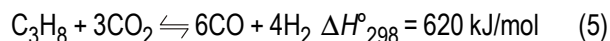


Fig. 2. (a) Equilibrium percentage conversion of propane, (b) equilibrium amount of propylene as a function of temperature and ratio of reactant gases for ODHP reaction.



The reforming of propane with CO_2 is a highly endothermic process and requires a stoichiometry of 1:3 ($\text{C}_3\text{H}_8:\text{CO}_2$). In particular, propylene formation (see Fig. 2) was significantly decreased for $\text{C}_3\text{H}_8:\text{CO}_2 > 1:2$ ratio due to the dominance of this reforming reaction. The formation of propylene goes through an optimum for 1:3 ($T = 800 \text{ K}$) ratio suggesting the occurrence of reforming reaction. The formation was further reduced with increase in CO_2 (1:4 ratio) and temperature of optimum was lowered by 50 K which could suggest the combined effect of reforming and RWGS, thereby significantly reduced the formation of propylene. Moreover, the formation of CO and propylene was ensured in ODHP and plotted in Fig. 3 for comparison. It is observed from Fig. 3 that upon increasing the CO_2 mole fraction at the inlet of RGibbs reactor increased CO but decreased propylene formation. This essentially confirmed that RWGS and propane reforming with CO_2 being the side reactions largely affect the desirable product (propylene) formation. Furthermore, it is evident from the results that the equimolar ratio of C_3H_8 and CO_2 would be ideal to achieve appreciable amount propylene. This reactant ratio can be used for experimental catalytic activity tests.

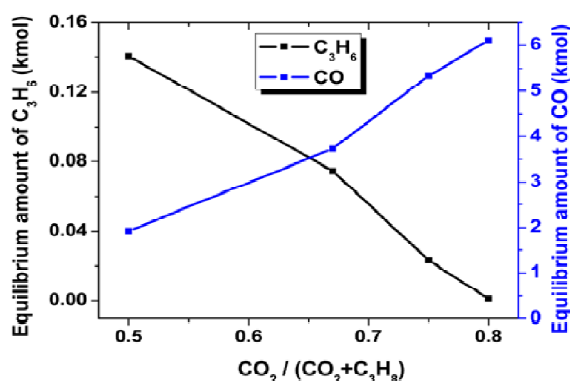


Fig. 3. Equilibrium composition of C_3H_6 and CO at $T = 820 \text{ K}$, $P = 1$ bar as a function of CO_2 mole fraction at the inlet of RGibbs reactor.

The effect of addition of inert into the equimolar feed was studied to observe any effect on propane conversion and propylene formation. The $X_{\text{eq},\text{C}_3\text{H}_8}$ and $n_{\text{eq},\text{C}_3\text{H}_6}$ were calculated at $T = 820 \text{ K}$ and $P = 1$ bar for three reactant ratio (1:1:1, 1:1:2, 1:1:3) and tabulated in Table 3. It is found that when inert N_2 was added on top of equimolar feed contain-

Table 3. Equilibrium propane conversion and propylene formation at $T = 820 \text{ K}$, $P = 1$ bar by adding inert N_2 to equimolar feed of C_3H_8 and CO_2 for ODHP reaction

$P_{\text{C}_3\text{H}_8}$ (bar)	$X_{\text{eq},\text{C}_3\text{H}_8}$ (%) ($\text{C}_3\text{H}_8:\text{CO}_2:\text{N}_2$)	$n_{\text{eq},\text{C}_3\text{H}_6}$ (kmol) ($\text{C}_3\text{H}_8:\text{CO}_2:\text{N}_2$)
0.33	48.7 (1:1:1)	0.16 (1:1:1)
0.25	51.0 (1:1:2)	0.18 (1:1:2)
0.20	53.0 (1:1:3)	0.20 (1:1:3)

ing C_3H_8 and CO_2 , the formation of propylene was favoured due to decrease in partial pressure of products. Zangeneh *et al.* reported similar increase in propane conversion in presence of inert or diluent³. It is observed from Table 3 that adding inert moles into the equimolar reactant system with CO_2 and propane increased the propane conversion and propylene formation to a smaller extent. Any further addition of inert is expected to cause similar slight increment due to further lowering of partial pressure. However, reactant ratio in the feed stream must comply with actual experiments using a catalyst and thus a suitable reactant ratio of 1:1:3 is suggested for experimental studies. The equilibrium amount of the products and reactants at this feed composition are shown in Fig. 4 over 600–1300 K. It is interesting to note that water is formed to a very small quantity and beyond 700 K the formation is almost negligible. This is due to the fact beyond 700 K, the DDP is more competitive than RWGS which is being a mild endothermic as compared to DDP, a strongly endothermic reaction. Therefore, H_2 is formed to a significant proportion along with increased propylene formation. It is thus evident that a feed stream containing propane, CO_2

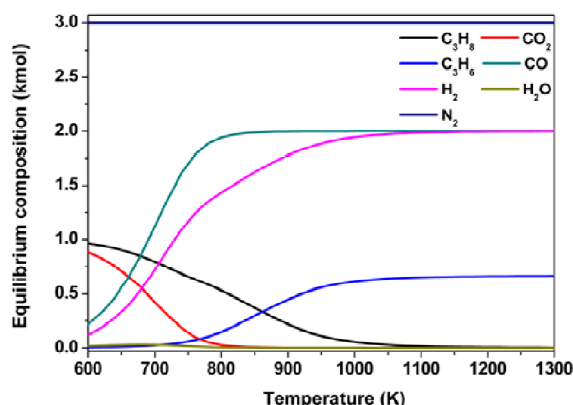


Fig. 4. Composition of reactant and products at equilibrium for $\text{C}_3\text{H}_8:\text{CO}_2:\text{N}_2 = 1:1:3$.

and N₂ in 1:1:3 ratio would theoretically produce appreciable quantity of propylene in the temperature range of 800–900 K. It must be mentioned that results of our current contribution initiated the in-depth understanding on finding the best operating condition which includes temperature, pressure, and reactant ratio for maximum propylene yield theoretically. And scope of improving this work lies on considering other possible products such as CH₄, C₂H₄ and carbon which are reported to be formed during experimental condition.

Conclusions

A preliminary study on the effect of increasing CO₂ and inert molecules, and temperature towards propylene formation in oxidative dehydrogenation of propane was conducted under the framework of thermodynamic equilibrium analysis. A suitable reactant ratio to be used in the feed stream during experiment was suggested which consisted of C₃H₈:CO₂:N₂ = 1:1:3. The excess CO₂ is not beneficial at least from a theoretical point of view as increase of which cause decreased propylene formation. Moreover, very high temperature owing to endothermic nature of this reaction is detrimental as desired product propylene is suffered due to formation of CO from undesired side reactions such as reverse water gas shift and reforming of propane.

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