

Catalytic dehydrogenation of light alkanes to high value chemicals

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Highlights

- A novel CrO_x based catalyst is developed for alkane dehydrogenation.
- Utilization of bio-genic CO₂ as a mild-oxidant in conjunction with propane feed under conditions of 1 atm and 610°C.
- Experimental findings indicate a 16% enhancement in propane conversion when employing CO₂, concomitantly augmenting the total olefin (ethylene + propylene) yields.

1. Introduction

Alkane dehydrogenation technology stands as a pivotal solution in meeting the escalating demand for petrochemical feedstock. However, inherent challenges such as low conversion rates and elevated operating temperatures impede its efficiency. Existing literature reveals a common trend of decreased conversion rates with the introduction of CO₂ as a co-feed alongside dehydrogenation processes [1]. In response to these challenges, our study introduces a novel CrO_x-based catalyst in conjunction with CO₂ feed to mitigate these limitations. Experimental investigations demonstrate a notable enhancement in propane conversion rates and overall olefin yield, offering promising avenues for advancing alkane dehydrogenation technology.

2. Methods

A CrO_x-based catalyst supported on SIRAL was synthesized via the sequential wetness impregnation technique. Extensive catalyst characterization was conducted to assess key parameters including surface area, pore volume, pore diameter and active sites. Subsequently, the catalyst was subjected to evaluation within a bench-scale fixed bed reactor, employing propane as the feedstock under varying conditions of temperature (ranging from 550°C to 630°C), pressure (1-atm), and Weight Hourly Space Velocity (WHSV) spanning 2 to 9 hr⁻¹, both with and without CO₂ as a co-feed. Analysis of the resulting product gas was performed using online Gas Chromatography (GC) techniques.

3. Results and discussion

In Figure-1 (a), the impact of Weight Hourly Space Velocity (WHSV) at 605°C on propane conversion, propylene selectivity, ethylene selectivity, and methane selectivity is depicted. The propane conversion remains relatively stable within the range of WHSV 2-3 hr⁻¹. However, with increasing WHSV values, conversion reduced to 27% at 8.8 hr⁻¹. Initially, selectivity remains relatively constant but marginally increases at higher WHSV. The increase in WHSV leads to a reduction in the residence time of reactants within the reactor, consequently diminishing the contact time and adversely affecting the conversion efficiency.

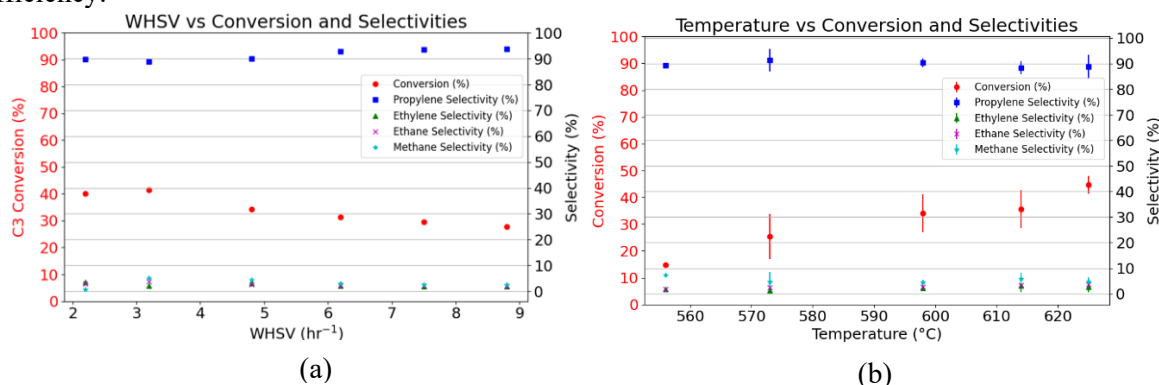


Figure 1: Variation of propane conversion and selectivity towards propylene, ethylene, and methane (a) with WHSV at 605°C and (b) with temperature at 4.5 hr⁻¹

Figure-1(b) demonstrates the impact of temperature on propane conversion and selectivity maintaining a constant WHSV of 4.5 hr⁻¹. The results show that with increasing temperature the conversion increases from 12% at 550°C to 44.7% at 625°C accompanied by a propylene selectivity of nearly 88%. Literature reported conversion of CrO_x on Al₂O₃ @ 550°C is 14% while the selectivity values are 95% [2]. For lower WHSV (<1 hr⁻¹), although the conversion increase from 36% to 48% the selectivity drops from 92% to 85%. Thus, the new catalyst showed better propane conversion and selectivity as reported in literature at higher WHSV as the support has a high alumina-silica ratio predominantly influenced by the alumina content. However, a marginal reduction in selectivity is due to methane formation during the dehydrogenation reactions which could be due to the acid sites inherent within the catalyst structure [3].

Table 1: Comparison of CO₂ assisted propane dehydrogenation vs direct dehydrogenation

Temp	WHSV	CO ₂ /C ₃	Propane	CO ₂	Propylene	Ethylene	CH ₄	CO
°C	hr ⁻¹		Conversion %		Yield %			
610	4	0	35.6	0.0	31.5	1.1	2.1	0
610	4	0.3	51.8	15.4	29.6	11.8	17.4	6.7

Table-1 presents the influence of CO₂ on propane conversion and selectivities of propylene and ethylene. The inclusion of CO₂ results in a notable 16% increase in propane conversion. However, there is a marginal decrease in propylene yield attributed to elevated ethylene and methane formation. Nonetheless, the total olefin yield (ethylene + propylene) rises from 32.6% to 41.4% upon CO₂ addition, owing to its function as a mild oxidant facilitating propane cracking. Nevertheless, the CO₂ hydrogenation reaction leads to the formation of a significant amount of methane. Given that the CO₂ source is biogenic, the nature of the resulting methane aligns with its green origins, thereby mitigating its classification as a pollutant. This biogenic syngas (methane+CO+H₂) byproduct holds potential utility as a green energy source.

4. Conclusions

Alkane dehydrogenation at reduced temperatures stands as a rapidly advancing area of sustainable research, driven by the imperative to mitigate environmental impact through diminished energy consumption and reduced CO₂ emissions. However, the inherently endothermic nature of the process poses a challenge, resulting in diminished olefin yields at lower temperatures. In the present work, we propose for the development of a novel catalyst and use of biogenic CO₂ as a mild oxidant in conjunction with propane feed. The data shows that this novel catalyst and CO₂ is able to increase the propane conversion while improving the total olefin yield. Additionally, our data suggests that ethylene production can be achieved at significantly lower temperatures compared to conventional ethane cracking methods, thereby highlighting the multifaceted benefits of incorporating biogenic CO₂ into the process. This utilization of CO₂ also results in production of biogenic syngas which underscores the environmentally sustainable nature of the process, further contributing to its green credentials.

References

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Keywords

Alkane dehydrogenation; Sustainability; CO₂ utilization.