

Propane to Light Olefins by One-Pot Cascade and Series Reactions

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Highlights

- Converting propane to light olefins via PDH/PTE reactions was investigated.
- Cascade & series PDH/PTE reactions were tested.
- Propylene was selectively converted to ethylene and butenes over P-ZSM-5.
- C₂₋₄ light olefin selectivities up to 88.5% were obtained.

1. Introduction

Light olefins such as ethylene and propylene are major large-volume commodity chemicals in the present petrochemical industry [1]. The dominant technology for the production of light olefins is the petroleum-derived naphtha cracking process [2]. Recently, the availability of considerable amounts of natural gas given the American shale-gas revolution has driven a shift to lighter, gas-based feed stocks; away from heavier oil-based feed-stocks in the petrochemical industry [3]. Among these light gas feedstocks, propane can be selectively converted to propylene via propane dehydrogenation (PDH) process. Nowadays, in a certain region of Asia, the price of propylene is cheaper than ethylene price because there are many propylene sources such as naphtha cracker, PDH, and methanol-to-propylene (MTP). However, propane thermal cracking exhibits lower light olefin yield and formation of plenty of methane compared with ethane steam cracking. Herein, production of light olefins from propane was investigated via cascade and series propane dehydrogenation/propylene-to-ethylene (PTE) reactions over highly selective two catalysts in the continuous fixed-bed reactor. The effect of reaction conditions also systematically studied with different reaction temperatures, space velocities, etc.

2. Methods

The PDH catalyst (20 wt% Cr₂O₃/Al₂O₃) was prepared by the simple incipient wetness impregnation method using aqueous solution of Cr(NO₃)₃·9H₂O. After impregnation, the sample finally calcined at 600 °C. For the preparation of the PTE catalyst (1 wt% P-ZSM-5), commercially available ZSM-5 zeolite (Si/Al₂ = 50, Zeolyst) was mixed with phosphoric acid in a solution of ethanol/water mixture, and the sample was then calcined at 500 °C. The catalytic performance was investigated using a quartz reactor in the lab-made fixed-bed reactor system. The PDH-PTE cascade reaction was carried out on two successive fixed beds of catalyst placed in the same reactor: the first consisted of 0.40 g of Cr₂O₃/Al₂O₃ and the second consisted of 0.50 g of 1 wt% P-ZSM-5. The PDH-PTE series reaction were performed using two separated fixed-bed reactor. The first fixed-bed reactor was with Cr₂O₃/Al₂O₃: the other fixed-bed was with 1 wt% P-ZSM-5. Before catalytic reaction, catalyst were pre-treated at 610 °C for 1 h.

3. Results and discussion

Fig. 1 (a) shows the catalytic results of cascade and series reactions over PDH and PTE catalysts. The lower propane conversion of the cascade reaction is due to the low reaction temperature (550 °C) compared with the series reaction (610 °C-550 °C). Both reactions shows the formation of ethylene from propylene over PTE catalyst, but the other by-products also produce, which were from oligomerization, hydrogenation, and cracking reactions. Fig. 1 (b) and (c) shows the catalytic results of the PDH-PTE cascade reaction with different temperatures and space velocities. As an increase of reaction temperature, the propane conversion and selectivities of methane and ethane also increase. In the lower space velocity at WHSV 1.2 h⁻¹, propane

conversion and selectivity of ethylene are higher than those of WHSV 17 h⁻¹. However, the selectivities of by-products are lower and the C₂₋₄ light olefin selectivities up to 88.5% were obtained.

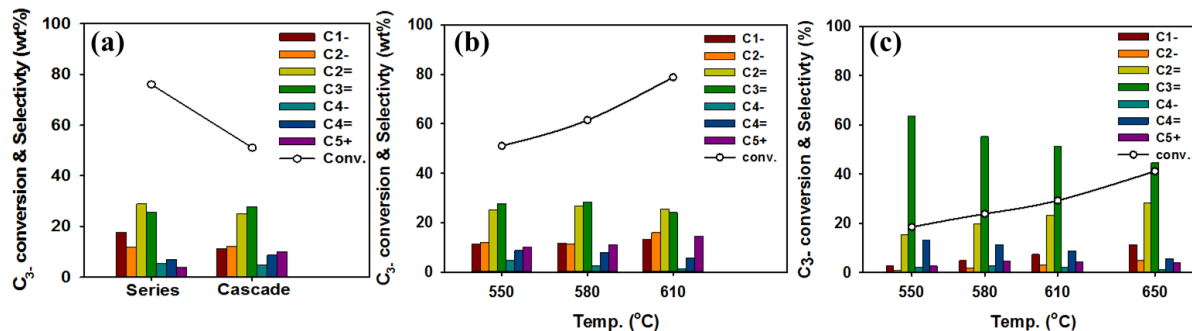


Figure 1. Catalytic results of (a) PDH-PTE cascade (550 °C) & series (610 °C-550 °C) reaction at WHSV 1.2 h⁻¹, and PDH-PTE cascade reaction at (b) WHSV 1.2 h⁻¹, and (b) 17 h⁻¹ with different reaction temperatures.

4. Conclusions

Converting propane to light olefins was investigated using two different PDH and PTE catalysts with cascade and series reactions. The propylene from the PDH reaction was selectively converted to ethylene and butene over P-ZSM-5 as the PTE catalysts at high space velocity and lower reaction temperature. The PDH-PTE cascade reaction showed high selectivities to C₂₋₄ light olefins up to 88.5%.

References

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Keywords

propane cracking; tandem catalysis; propane dehydrogenation; propylene-to-ethylene.