

Production of Olefins via Oxidative Dehydrogenation of Simple Refinery Alkanes in the Presence of H₂S

Zahra A. Premji¹ and P.D. Clark^{2*}

¹University of Calgary, Calgary, Alberta T2N 1N4 (Canada)

² Alberta Sulfur Research Ltd., University Research Centre,
Calgary, Alberta T2L 2K8 (Canada)

*pdclark@ucalgary.ca

Introduction

The project will examine the oxidation of C₃ to C₅ alkanes in the presence of H₂S, as individual components, then as mixtures to form olefins. Light unsaturated hydrocarbons such as propylene and butylenes are important feedstocks used in the manufacturing of high octane gasoline, chemicals and polymers. Examples of large-scale uses of propylene are in the manufacturing of polypropylene, acrylonitrile and propylene oxide. Majority of the production of propylene in the petrochemical industry is currently carried out by thermal and catalytic cracking processes in refineries [1]. These processes suffer from low yields as the propylene produced is a co- or by-product of the reactions. The processes are endothermic, consuming high amounts of energy and produce a significant amount of undesirable products such as carbon dioxide, a known green-house gas.

Catalytic oxidative dehydrogenation has the potential to overcome some of the limitations of current methods for olefin production and has therefore been investigated extensively for the production of propylene [2, 3], however the yields obtained to date have been too low to satisfy industrial requirements. Currently, the main advantage to this process is that it is exothermic and therefore requires a relatively lower input of energy. However, it is known to suffer from thermodynamic limitations as the products are more reactive than the reactants and therefore undergo further oxidation. Over-oxidation of the products is a common problem and leads to the production of carbon oxides. In order to tackle the problem of over-oxidation, a compound such as H₂S could be used in conjunction with oxygen providing sulfur species which act as O₂ transfer agents. This strategy might prevent the over-oxidation that occurs thus improving the selectivity and yield of the products.

Materials and Methods

To carry out the investigation, a feed gas containing the appropriate alkane, oxygen, H₂S and N₂ would be passed across a catalyst bed contained in a heated reactor. To prevent pre-mixing of the alkane and oxidant, the gases are fed through two different tubes and then mix at the head of the catalyst bed. The different parameters including gas composition, temperature, residence time as well as the catalysts used will be varied to find the optimal operating conditions for the conversion to olefins and to gain a deeper understanding of the effect of each of the variables and how they influence the chemistry of the process. The catalysts to be investigated for this reaction are transition metal oxides such as vanadium, niobium or molybdenum oxides on various porous supports such as silica or MCM-41.

The catalytic supports will be obtained commercially if possible, or synthesized in the lab when unavailable, using procedures obtained from the literature. Wet impregnation of the

active species such as vanadium oxide will be carried out in the laboratory followed by calcination to obtain the final catalyst. The catalysts made will be analyzed for surface area using a catalyst characterization instrument. Active species loading will be confirmed using complete acid digestion followed by ICP analysis. Some of the catalyst characterization methods mentioned above will also be carried out on the spent catalyst to determine the degradation, if any, of the catalysts after an experiment. The product gas will be analyzed using gas chromatography to determine the conversion, selectivity and yield for the process. As well, surface species analysis of the catalysts will be carried out to provide information on the interactions between reactants and the catalytically active species.

Results and Discussion

The preliminary results show the beneficial effect of H₂S in the reactant gas stream. As can be seen from Table 1 below, the selectivities to propylene, for similar propane to oxygen ratios in the presence and absence of H₂S, are enhanced when H₂S is present. There is a greater than 45% increase in propylene selectivity (compare row 1 and 2) when H₂S is added to the reaction gas stream while keeping the overall propane to oxygen ratios the same.

Table 1. Conversion of propane and selectivities of C₃ and C₂ olefins in the short contact time (5 ± 0.5 ms) ODH of propane over quartz chips.

| Feed gas composition C ₃ H ₈ : H ₂ S : O ₂ | Conversion (%) | Selectivities (%) | | T (°C) |
|---|----------------|-------------------------------|-------------------------------|--------|
| | | C ₃ H ₆ | C ₂ H ₄ | |
| 4:0:1 | 69.40 (±0.14) | 18.39 (±0.03) | 37.35 (±0.08) | 700 |
| 4:2:1 | 63.74 (±0.45) | 26.60 (±0.22) | 19.15 (±0.15) | 700 |
| 2:0:1 | 88.30 (±1.0) | 11.51 (±0.62) | 36.78 (±0.22) | 700 |
| 2:1:1 | 82.60 (±0.74) | 27.20 (±0.76) | 25.72 (±0.16) | 700 |

These preliminary results show that the presence of H₂S reduces cracking and promotes oxidative dehydrogenation hence leading to lower selectivities to cracking products (i.e. ethylene) and higher selectivity to dehydrogenation products (i.e. propylene). Catalytic work based on silica catalysts will also be presented in the poster.

Significance

The production of olefins by oxidative dehydrogenation has been investigated extensively for the ultimate purpose of building units designated solely for their use in meeting the growing demand for olefins. However, selectivity issues at high conversion have made this impossible for propylene production to-date. For this reason, innovative selectivity improvements are still being sought, as well; gaining a better insight into the effects of the various parameters will help with the ultimate design and operation of such a unit, if the results can meet industrial standards.

References

1. G.A. Olah, A. Molnar, Hydrocarbon Chemistry 2nd Ed., Wiley-Interscience, Hoboken, NJ, 2003.
2. Parmaliana, A., Sokolovskii, V., Arena, F., Frusteri, F., and Miceli, D. *Catal. Lett.* 40, 105 (1996).
3. Kondratenko, E.V., Cherian, M., and Baerns, M. *Catal.Today* 112, 60 (2006).