Electrocatalytically-assisted Oxidative Dehydrogenation (ODH) of Lower Alkanes to Olefins

Anshuman Fuller¹, Doruk Dogu¹, Katja E. Binkley¹, Nathaniel Kramer¹, Anne Co² and Umit S. Ozkan³

¹William G. Lowrie Department of Chemical and Biomolecular Engineering, The Ohio State University, Columbus, Ohio 43210 (USA)
²Department of Chemistry, The Ohio State University, Columbus, Ohio 43210 (USA)
³ozkan.1@osu.edu

Introduction

Alkane ODH is an important catalytic reaction for converting lower alkanes to olefins, such as ethylene and propylene. However, one of the shortcomings of traditional ODH is the limited ability to prevent further oxidation of the formed olefins to carbon oxides [1]. Novel reactors using an oxide ion-conducting membrane offer a potential solution to control the selectivity to the desired olefins by regulating the availability of oxygen to the alkane [2, 3]. These reactors are similar to the setup of solid oxide fuel cells, but instead of generating power, an external voltage/current is applied to control the oxygen supply to the alkane. This can potentially help regulate the extent of alkane conversion and enhance the selectivity towards partial oxidation products. Initial electro-catalytic reaction tests an Au electrode demonstrated the feasibility of such a reactor. The currents studies are focusing on developing Ti-based perovskites to be tested as electro-catalysts for this application.

Materials and Methods

O₂ flux tests (from 550-700°C) and electrocatalytically-assisted ODH tests were conducted in an electrochemical reactor consisting of a yttria-stabilized zirconia (YSZ) membrane, sandwiched between an Au anode and an LSM (Lanthanum strontium manganite) - YSZ composite cathode. Helium was flowed for flux measurements, while 5% ethane in helium was flowed on the anode side for the ODH tests. The cathode was exposed to stagnant air. The cell was sealed with the help of Aremco 617 glass sealant. A Keithley current source was used to apply current and the reactor effluent was monitored using a Shimadzu GC 2014.

Results and Discussion

Oxygen flux tests (Figure 1) displayed a good match between the actual and predicted O₂ flux values (by Faraday’s Law, Flux = Current/ 4F) up until 5mA for all temperatures. At 550°C and 600°C for currents higher than 5mA, a deviation was observed pointing to the limited transfer of oxygen ions across the electrolyte. The actual O₂ flux at 700°C was higher than at 550°C and 600°C and closely followed the ideal values, due to the increased oxide ion conductivity at that temperature. This confirms the reactor’s ability to regulate oxygen amount as a function of applied current.

Preliminary electrocatalytic ODH tests with the same cell at 550°C (Figure 2) demonstrated increased (and preferential) ethylene formation with applied current, whereas CO₂ production did not exhibit any such trend. It is likely that the electrochemically-pumped oxygen species lead to the production of partial oxidation products and limit complete oxidation. The low H₂ formation rates at all currents, confirm that most of the ethylene produced results from the ODH reaction as opposed to non-oxidative dehydrogenation reaction. These results at 550°C are promising and display the feasibility of controlling reaction selectivity in such a reactor. Further tests with reactors having Ti-based perovskite electrocatalysts (LSTs) on the anode, will be performed.

Figure 1: O₂ flux tests for a cell with Au| YSZ| LSM-YSZ from 550-700°C (active area of cell: 0.5cm²)

Figure 2: Electrocatalytic ODH tests with an Au| YSZ| LSM-YSZ cell at 550°C

Significance

Converting lower alkanes to olefins is expected to grow in importance as shale gas production begins to increase. Being able to selectively produce them through electrocatalytically assisted ODH of abundant and cheap feedstocks such as ethane and propane holds great promise. However, research into designing the most active and selective electrocatalysts still needs to be conducted.

References: