

PRODUCTION OF LIGHT ALKENES BY A MULTI-STEP OXIDATIVE DEHYDROGENATION IN A NOVEL PEROVSKITE HOLLOW FIBER MEMBRANE REACTOR

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Summary

A membrane reactor incorporating a hollow fiber with successive parts of oxygen permeable and passivated surface segments has been developed and was used for the oxidative dehydrogenation of ethane and propane. This membrane geometry allows a controlled oxygen feeding into the reactor over its axial length. In the oxidative dehydrogenation, the thermodynamic limitation of alkane dehydrogenation can be overcome. By using this novel hollow fiber membrane reactor with a dehydrogenation catalyst, oxygen separation and alkene formation could be established even at temperatures as low as 625 °C with long-term stability. The performance of this reactor is evaluated by applying various reaction conditions.

Keywords

novel reactor technologies, membrane reactors, sustainability

Introduction

Steam cracking of hydrocarbons is the most important process for the production of light alkenes although it is a highly endothermic process with extensive coke formation that suffers from thermodynamic limitation. One concept to overcome the latter is the oxidative dehydrogenation of hydrocarbons (ODH), where alkane and oxygen are co-fed and give rise to the olefin and water. The main problem encountered in ODH is the presence of the consecutive reaction of olefin combustion, e.g. deep oxidation into carbon dioxide and water as well as partial oxidations or thermal cracking at higher reaction temperature that rapidly decreases the olefin yield when the conversion of the alkane is increased.

Our group has presented the use of a dense mixed

oxygen ion and electron conducting (MIEC) perovskite hollow fiber membrane of the composition $\text{BaCo}_x\text{Fe}_y\text{Zr}_z\text{O}_{3-\delta}$ (BCFZ, $x+y+z=1$), e.g. for the direct decomposition of nitrous oxide to nitrogen by in situ oxygen removal¹ and the simultaneous production of hydrogen and synthesis gas by combining water splitting with partial oxidation of methane². In this work the BCFZ hollow fiber membrane is introduced for the oxidative dehydrogenation of ethane (ODE) and propane (ODP)^{3,4}. In our concept the dehydrogenation (DH) of the alkane $\text{C}_m\text{H}_{n+2} \rightleftharpoons \text{C}_m\text{H}_n + \text{H}_2$ occurs in a first reaction zone without addition of oxygen followed by the selective combustion (SC) of hydrogen $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$ with oxygen delivered through the membrane (Fig. 1).

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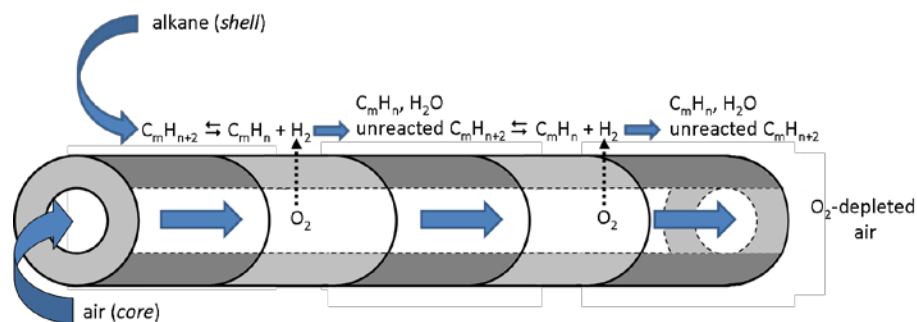


Fig. 1: Schematic diagram of the concept for the stepwise oxidative dehydrogenation of light alkanes.

Experimental

The manufacture of the hollow fiber membrane of the composition $\text{BaCo}_x\text{Fe}_y\text{Zr}_z\text{O}_{3-\delta}$ (BCFZ, $x+y+z=1$) is described elsewhere⁵. The fibers were coated with gold paste to obtain five permeation zones alternating with passivated areas (Fig. 2). The coated membranes were

inserted into a porous alumina tube to avoid direct contact with the dehydrogenation catalyst (Cr_2O_3 for ODE, Pt/Sn for ODP), which was dispersed between the inner porous alumina tube and an outer dense alumina tube.

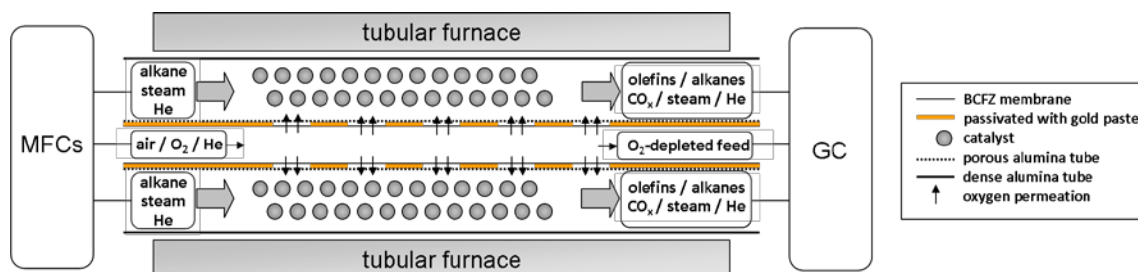


Fig. 2: Scheme of the membrane reactor for the stepwise oxidative dehydrogenation of light alkanes.

Results

Our membrane reactor using a dehydrogenation catalyst can compete with the best catalysts used in the co-feed mode of the ODP and in the range of low and moderate ethane conversions of the ODE (Fig. 3). The

membrane not only separates the hydrocarbon feed from oxygen but also avoids the need of an oxygen separation plant. Ongoing TAP-experiments will provide a deeper insight into the molecular mechanisms.

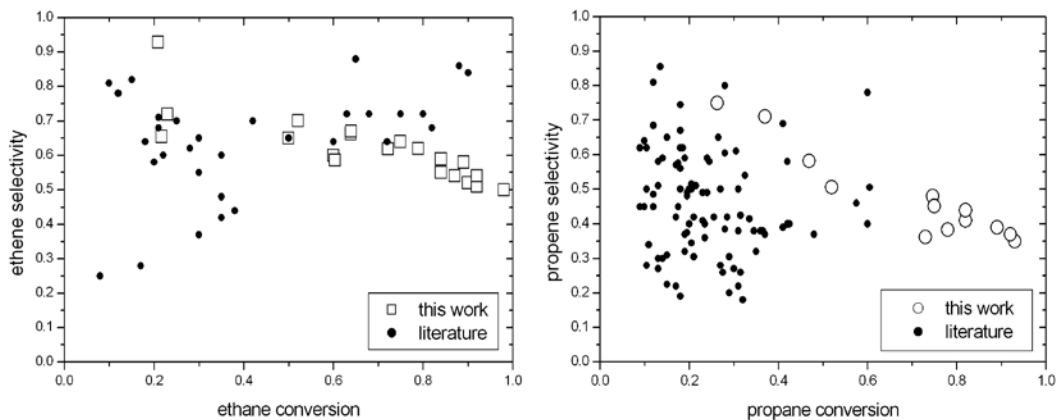


Fig. 3: Ethene (left) and propene (right) selectivity as a function of ethane and propane conversion, respectively. The data for various catalytic systems reported in the literature between 2000 and 2006 were taken from⁶.

Acknowledgment

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