Continuous oxygen ion transfer medium as a catalyst for high selective oxidative dehydrogenation of ethane

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An oxygen permeable mixed ion and electron conducting membrane (OPMIECM) was used as an oxygen transfer medium as well as a catalyst for the oxidative dehydrogenation of ethane to produce ethylene. O$_2^-$ species transported through the membrane reacted with ethane to produce ethylene before it recombined to gaseous O$_2$, so that the deep oxidation of the products was greatly suppressed. As a result, 80% selectivity of ethylene at 84% ethane conversion was achieved, whereas 53.7% ethylene selectivity was obtained using a conventional fixed-bed reactor under the same reaction conditions with the same catalyst at 800 °C. A 100 h continuous operation of this process was carried out and the result indicates the feasibility for practical applications.

KEY WORDS: dehydrogenation; oxygen separation; membrane reactor; ethane; ethylene.

1. Introduction

In the petrochemical industry, more than 60% of products obtained by catalytic processes, including some huge commercial processes such as oxidation of $n$-butane to maleic anhydride, are produced via oxidation [1,2]. The difficulties in this process lie in the fact that intermediates and target products, *i.e.*, olefin and oxygenates, are usually more reactive than the raw materials; alkanes, therefore, are easily deeply oxidized to CO$_2$. As a result, the selectivity for the target products is significantly lowered. Alternatively, peroxides, such as hydrogen peroxide [3], alkyl hydroperoxides or iodosylbenzene [4], are used as oxidants to control the deep oxidation of products. However, these peroxides are expensive and their production is harmful to the environment. Therefore, the most attractive oxidant for the chemical industry is molecular oxygen, O$_2$, because of its low cost and less environmental contamination. The crucial step in using O$_2$ as an oxidant is to prevent the products from being deeply oxidized by this oxidant. Several experiments were reported up to date on protecting reactants from being attacked directly by O$_2$. One reduced the contact time between O$_2$ and reactants to less than $10^{-3}$ second in order to prevent further oxidation of the products [5–7]. The other employed a regioselective catalyst to terminally oxidize the linear alkanes by O$_2$ [8]. A successful industrial processing example is the use of a metal oxide as an oxygen transfer agent in a periodic shift reactor, which has been used in the ammoxidation of propylene to acrylonitrile [9] and of metaxylene to isophthalonitrile [10]. In these reactions, the metal oxide participates in a series of redox steps. This reaction strategy results in a higher selectivity in comparison with the conventional method in which hydrocarbon and oxygen are simultaneously in contact with an oxidation catalyst. However, these processes can only be operated periodically, and a catalyst that is physically and chemically more stable is to be developed to sustain repeated reduction-oxidation cycles [11].

We report the results of the oxidative dehydration of ethane to produce ethylene using an oxygen permeable mixed ion and electron conducting membrane (OPMIECM) [12–22]. The mechanism of our reaction process is shown in figure 1. Molecular O$_2$ (in air) at the air side of the OPMIECM obtain electrons from the surface of the OPMIECM to form O$_2^-$ species (lattice oxygen). Sequentially, the lattice oxygen is transported through the OPMIECM to the reaction side. Once the reaction side is reached, lattice oxygen will react quickly with ethane on the surface of the OPMIECM before it recombines to molecular oxygen. Local charge neutrality is maintained by the joint diffusion of oxygen vacancies and electrons. Since lattice oxygen converted from O$_2$ by the OPMIECM is continuously supplied to the reaction system, the selectivity of the oxidation reaction can be controlled at a very high level.

2. Experiments

Our OPMIECM reactor is illustrated schematically in figure 2. The material of the OPMIECM is Ba$_{2}$Sr$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ recently developed in our laboratory. A more detailed synthesis process can be
found in our previous papers [23,24]. The permeation area of the OPMIECM disk is 0.813 cm². 10% C₂H₆ + 90% He was fed to the reaction side, while air was fed to the air side. The inlet gas flow rates were controlled with mass flow controllers (models D07-7A/ZM). Both reaction side and air side of the reactor were maintained at atmospheric pressure. The online gas chromatograph (HP6890) was equipped with two automatic valves, a sample valve and a bypass valve, and the HP Chemstation computer software for data collection and analysis. A serial/bypass configuration was arranged for two isothermal columns (80°C), Porapak Q and molecular sieve 13X. The injection of sample gases directed the mixture of H₂, O₂, N₂, CH₄, CO, CO₂, C₂H₄ and C₂H₆ through the Porapak Q. H₂, O₂, N₂ and CO were eluted earlier than CH₄, CO₂, C₂H₄ and C₂H₆ from the Porapak Q column and then quickly entered the serial-arranged molecular sieve 13X column. Before the H₂, O₂, N₂ and CO were eluted from the molecular sieve 13X column, a bypass valve was activated to deaden the 13X column and direct the outlet of the Porapak Q column to the thermal conductivity detector. Once CH₄, CO₂, C₂H₄ and C₂H₆ had eluted from the Porapak Q, the valve was again activated, and the H₂, O₂, N₂ and CO were eluted from the molecular sieve column 13X to the detector. An external standardization was used for product analysis. Multiple-point calibration curves were created and recalibrated routinely for long-term studies. The quantity of H₂O was calculated by hydrogen atomic balance. The oxygen permeation rate was calculated from the measured outlet flow rate and the mole fractions of oxygen-containing product gases, such as CO, CO₂, O₂ and H₂O. The carbon balance during all of the experiments was within 5%. The separation of O₂ and N₂ was crucial for leak checking on the membrane tube and the sealing. The leakage of oxygen could be calculated from the leakage of nitrogen. In the reaction experimental results, the leakage of oxygen, which accounted for 0 to 2% of the total oxygen flux, was subtracted from the total oxygen flux.

3. Results and discussion

The intrinsic catalytic behavior of the OPMIECM reactor based on BSCFO for oxidative dehydrogenation of ethane to ethylene was performed in the reactor, as shown in figure 2. After sealing at high temperature (1040°C), the furnace was cooled down to the temperatures of interest, then air was introduced to the air side and the feed (10% C₂H₆ + 90% He) was introduced to the reaction side. In all the experiments, air flow rate was 300 ml/min. The species detected in the eluted gas of the reaction side were C₂H₄, C₂H₆, H₂O, CO₂, CO and CH₄. There was no O₂ detected in the eluted gas, which indicated that O₂ was consumed completely in this reaction. Figure 3 shows the temperature effect on the performance of oxidative dehydrogenation of ethane to ethylene in the OPMIECM reactor when the feed flow rate was kept constant at 30 ml/min. As shown in figure 3, with the increase of reaction temperature from 700°C to 850°C, the C₂H₆ conversion increased from 18.0% to 96.5%, the C₂H₄ selectivity decreased from 91.0% to 60.2%, and the yield of C₂H₂ reached the maximum value (67.4%) at 800°C, then decreased slightly between 800°C and 900°C. The oxygen permeation of the membrane increased with the increase of temperature, and the oxygen permeation flux in Air/C₂H₆-He gradient (Jₒₒ = 1.72 ml/cm² min, at 800°C) is about two times that in Air/He gradient (Jₒₒ = 1.0 ml/cm² min, at 800°C). However, when we