Olefin production by a two-step oxidative dehydrogenation in a novel perovskite hollow fiber membrane reactor

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Introduction

Since the chemical industry depends on ethene as a feedstock, there is a high motivation to study methodologies for the conversion of ethane to ethene. The latter is currently produced by the thermal cracking [1], which is a highly endothermic process with extensive coke formation. The oxidative dehydrogenation of ethane to ethene (ODE), where ethane reacts directly with surface oxygen according to $C_2H_6 + ½\ O_2\ (s) \rightarrow C_2H_4 + H_2O$ is considered as an alternative to the current cracking process [2]. No thermodynamic limitation of the conversion, lower temperatures as well as less coke formation are expected. In order to increase the selectivity for ethene, a controlled contact mode is necessary. A dense mixed oxygen ion and electron conducting perovskite hollow fiber membrane offers a beneficial contact medium for the ODE. In our case, in a first step a catalytic dehydrogenation according to $C_2H_6 \rightarrow C_2H_4 + H_2$ takes place followed by the selective oxidation of hydrogen according to $H_2 + ½\ O_2 \rightarrow H_2O$.

Materials and Methods

The fabrication of the hollow fiber membrane of the composition $BaCo_xFe_yZr_zO_{3-\delta}$ (x+y+z=1) is described elsewhere [3]. To shorten the contact time in order to avoid the deeper oxidation of ethene/ethane to CO and CO_2, the fiber was coated with gold except on a length of 4 cm in the isothermic hot zone of the oven. The membrane was inserted into a porous alumina tube. On the outside, a dehydrogenation catalyst (Cr_2O_3 on Al_2O_3) was dispersed as shown in Figure. 1. For the ODE, ethane diluted with steam, in order to increase the driving force to conversion by decreasing the partial pressures, was fed to the shell side, while air was fed to the core side.

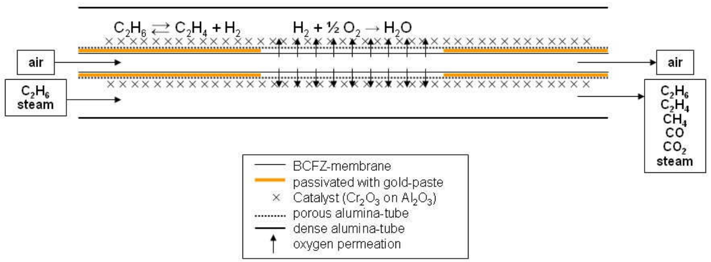
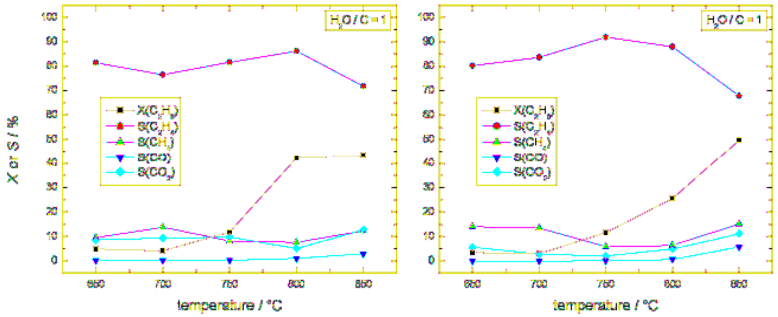


Figure 1. Schematic diagram of the hollow fiber membrane reactor for the ODE.

Results and Discussion

Figure 2 shows the ethane conversion *X* and product selectivities *S* as a function of the oven temperature. In 2 (a) (F_{core} = 200 mL·min^{-1} air, F_{shell} = 20 mL·min^{-1} C_2H_6, 40 ml min^{-1} steam, 0.5 mL·min^{-1} Ne) where a steam to carbon ratio of 1 was applied, the ethane conversion increased from 5 to 43 % whereas the ethene selectivity ranged from 72 to 86 %. When the air flow rate was reduced by half at a steam to carbon ratio of 1, the ethane conversion even increased from 3 to 50 % while the ethene selectivity ranged from 68 to 92 % (Figure 2 (b)). Both, a catalytic dehydrogenation followed by a selective catalytic hydrogen combustion with comparable yields and selectivities is reported by Grasselli et al. [4]. However, in our case no periodic regeneration is necessary. Moreover, the ethene selectivitiy could be increased in comparison to earlier experiments [5], although the ethane conversion still needs to be improved. In further experiments the reaction conditions for the described membrane reactor as well as for other catalysts (e.g. VO_x) have to be optimized



(a) **(b)**

Figure 2. Effect of the temperature on the ethane conversion *X* and product selectivities *S* for a steam to carbon ratio of 1. In experiment (a) an air flow rate of 200 mL·min^{-1} was applied, whereas in experiment (b) the air flow rate was 100 mL·min^{-1}.

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