SIMULTANEOUS PRODUCTION OF ETHYLENE AND SYNGAS BY COMBINING OXIDATIVE COUPLING AND REFORMING OF METHANE IN A MEMBRANE REACTOR

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With the rapid consumption of the world oil reserves, it is expected that natural gas will more and more become a widely used source of chemicals. Bulk chemicals like ethylene with an annual production of 20,000-30,000 metric kilotons in Europe are currently mainly produced from crude oil via a cracking route. Direct conversion of natural gas into ethylene and ethane can be achieved by oxidative coupling of methane (OCM), at relatively high temperatures (above 750 °C). Despite large efforts from many researchers, the maximum single-pass C_2 yield on the best catalysts is limited to only about 15-20% due to undesired combustion reactions, deteriorating the selectivity to C_2's (Choudhary and Uphade, 2004). However, if the mixture of by-products from the OCM reactions, typically CO, CO_2, H_2 and H_2O (see Fig. 1), could be shifted and reformed with methane to synthesis gas, two major advantages can be achieved in one stroke: Firstly, the overall methane conversion can be increased producing C_2's and synthesis gas simultaneously, where the produced synthesis gas can be used for the production of synthetic fuels via the Fischer-Tropsch process. Concurrent production of ethylene and synthesis gas is particularly interesting, because the C_2 fraction that can be produced in the Fischer-Tropsch process is relatively low compared to the demand for C_2's. Secondly, by combining the oxidative coupling and steam and dry reforming of methane an overall autothermal process can be achieved. The challenge is to introduce a reforming catalytic activity in such a way that the reaction rates of the exothermic OCM and the endothermic reforming reactions are balanced to create an autothermal process (see Fig. 1).

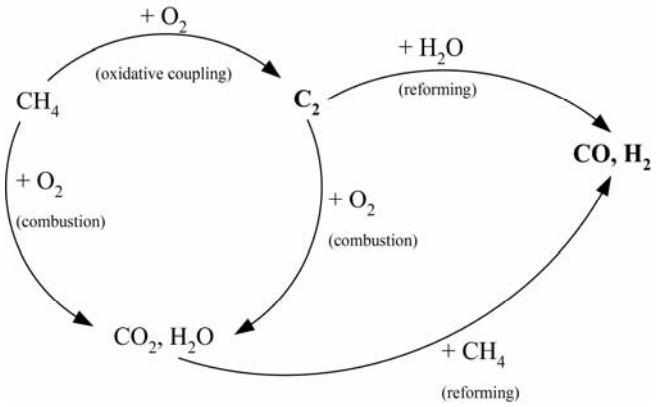

Figure 1: Overall reaction scheme for the combined OCM and SR process.

To arrive at autothermal operation, the total C_2 selectivity at higher methane conversions needs to be increased to obtain a yield of approximately 30%. Since the catalytic route already is optimized to a large extent, a combination of a stable and selective catalyst with operation at low O_2 concentrations is used to enhance the overall C_2 selectivity. In this research it is investigated whether application of a packed bed membrane reactor to

distributively dose oxygen along the axial coordinate leads to increased selectivity at high CH_4 conversion. It has already been shown that application of packed bed membrane reactors for OCM with porous membranes indeed show a higher selectivity towards C_2 products at comparable methane conversion levels compared to co-fed fixed bed reactors (Coronas et al., 1994; Tonkovich et al., 1996). Moreover, distributed feed of oxygen or air will lead to a more uniform temperature profile, decreasing unselective gas phase reaction rates. With an isothermal plug flow packed bed membrane reactor model, where O_2 was uniformly distributed along the reactor length, it was verified that lowering the overall oxygen concentration indeed leads to an increase in the overall C_2 yield and hence selectivity (see Fig. 2). Even more interestingly, it is shown that the optimal C_2 yield is reached at higher CH_4 conversions when operating at lower O_2 concentrations.

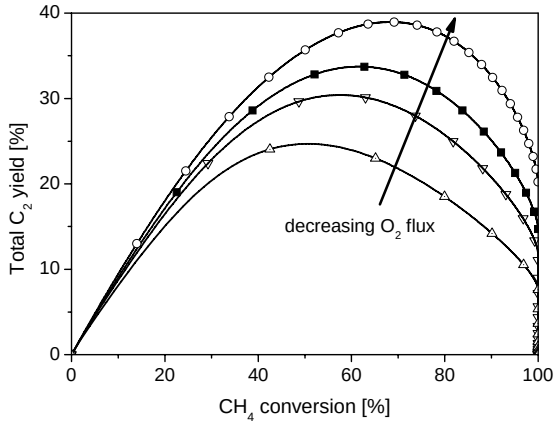

Figure 2: reactor model simulations overall C_2 yield in a membrane reactor at constant O_2 flux (T=825°C).

Although the packed bed membrane reactor models predict C_2 yields of more than 30%, during experiments under similar conditions the measured selectivity and yield was much lower than predicted. Comparison between experimental results and simulation data in the literature also reveals that theoretical models overestimate the overall yield of higher hydrocarbons produced (Liu et al., 2001).

In this work it is investigated whether distributed dosing of O_2 along the axial coordinate leads to significant enhancement of overall C_2 selectivity at higher methane conversions. A shell and tube membrane reactor equipped with porous membranes was used to perform experiments on a $Mn/Na_2WO_4/SiO_2$ catalyst (Fang et al., 1992). Experimental results for different overall O_2 permeation fluxes and operating conditions (T = 700-900°C, p = 1-2 bara) are compared with simulation data. Based on the gained insights, the integrated steam reforming and oxidative coupling of methane in an autothermal membrane reactor will be studied.

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