OXIDATIVE COUPLING OF METHANE IN A SOLID OXIDE FUEL CELL REACTOR

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A novel gas-recycle solid oxide fuel cell reactor-separator has been developed which gives very high ethylene yields during the oxidative coupling of methane. The recycled gas passes continuously through a molecular sieve trap in the recycle loop, which traps and thus protects an easily controllable percentage (up to 100%) of C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{6} produced during each gas cycle. The C\textsubscript{2} products are obtained by subsequent heating of the molecular sieve trap. Ethylene yields up to 85% (88% C\textsubscript{2}H\textsubscript{4} selectivity at 97% methane conversion) were achieved using a Ag or Ag-Sm\textsubscript{2}O\textsubscript{3} anode during batch operation under conditions of chemical cogeneration.

INTRODUCTION

Since the seminal work of Keller and Bhasin (1) on the catalytic one-step oxidative dimerization or "coupling" of methane (OCM) to C\textsubscript{2} hydrocarbons, ethane and ethylene, numerous catalysts have been found which give selectivities to C\textsubscript{2} hydrocarbons higher than 90% at low (<2%) methane conversion. However, it was universally found that the total C\textsubscript{2} hydrocarbon selectivity decreases drastically with increasing conversion of methane, so that Y\textsubscript{C\textsubscript{2}} (the total C\textsubscript{2} hydrocarbon yield) was always found until very recently to be less than 30% (1-9). This also includes SOFC units with various anodic electrocatalysts which have also been investigated extensively for the OCM reaction (6). Such units offer the advantage that oxygen is not admixed with methane and with the OCM products and thus the complete oxidation reaction can in principle be suppressed. Achieving C\textsubscript{2} hydrocarbon yield in excess of 50% is a necessary requirement for the development of an economically viable industrial process.

The reason for the low C\textsubscript{2} selectivity values at high methane conversion C\textsubscript{CH\textsubscript{4}} and thus the reason for the low measured Y\textsubscript{C\textsubscript{2}} and Y\textsubscript{C\textsubscript{2}H\textsubscript{4}} yield values of earlier studies (1-9) is that the desired products, ethylene and ethane, are far more reactive with oxygen than methane and therefore are easily oxidized to CO/CO\textsubscript{2} when their concentrations become comparable to that of methane, i.e. for high methane conversion. Aris and coworkers (10) recently showed that Y\textsubscript{C\textsubscript{2}} and Y\textsubscript{C\textsubscript{2}H\textsubscript{4}} can be increased up to 50% and 17%, respectively, by using a Sm\textsubscript{2}O\textsubscript{3} catalyst in a simulated countercurrent moving bed chromatographic reactor (SCMBCR) to carry out the OCM reaction. The observed significant improvement in C\textsubscript{2} yield (~50%) in the case of the
SCMBCR is due to the partial separation and removal of C₂ hydrocarbons from unreacted methane and oxygen. Despite the reactor complexity, which may not be easy to adapt to industrial practice (11), this pioneering work created a great deal of interest (11).

We have now found a means to almost entirely eliminate the problem of the high reactivity of the C₂ hydrocarbons during the OCM reaction by using a gas recycle solid oxide fuel cell reactor, with a Ag or Ag-Sm₂O₃ anode, combined with an appropriate molecular sieve trap in the recycle loop (Linde molecular sieve 5A maintained at <70°C) which traps and thus protects an easily controllable percentage (up to 100%) of ethylene and of ethane produced during each gas cycle (12). An important feature of this molecular sieve material is that it traps ethylene much more effectively than ethane and thus leads to very high ethylene yields (up to 85% in this work). The process is simple and appears promising for industrial applications (13). In this paper we summarize some key results of our previous work (12) and discuss some aspects relevant to chemical cogeneration in SOFC units (14).

**EXPERIMENTAL**

The recycle reactor is shown schematically in Figure 1. It consists of an SOFC reactor with a Ag or Ag-Sm₂O₃ anode and a Ag cathode or of a fixed bed catalytic reactor with a bypass loop, a recycle pump and a molecular sieve trap unit. The latter comprises one or two packed bed columns in parallel each containing 2-10 g of Linde 5A molecular sieve pellets. On line gas chromatography was used for the analysis of CH₄, O₂, CO, CO₂, C₂H₄ and C₂H₆ in the reactants and products.

Two types of reactors were used: One was a CSTR type SOFC consisting of a Y₂O₃ (8mol%)-stabilized ZrO₂ (YSZ) tube (length 15 cm, diameter 2 cm) closed flat at one end with an appropriately machined water-cooled stainless steel reactor cap attached to the other end, thus allowing for continuous gas feed and removal (12,14). In this reactor the catalyst was a porous Ag or Ag-Sm₂O₃ film (mass, 150 mg; superficial surface area, 10cm²) coated on the inside walls of the O²⁻-conducting YSZ tube (Fig.1). Catalyst preparation is described elsewhere (12).

The second reactor was a plug flow quartz reactor (length 10 cm, diameter 1 cm) with a fixed catalyst bed of Sr(1wt%)/La₂O₃ pellets (0.5-1mm diameter, total mass 0.5g). Results of this investigation have been presented elsewhere (15).

The SOFC CST reactor was operated at temperatures 780° to 830°C. A galvanostat was used to control constant currents I between the catalyst and a counter electrode deposited at the outer walls of the YSZ tube. In this way, oxygen is supplied to the Ag-based catalyst at a rate I/2F mol O/s, where F is Faraday’s constant. The SOFC reactor was operated only under conditions of chemical cogeneration (14,16,17) i.e. with the anode potential negative (by 0.4 to 0.1 V) with respect to the cathode, so
that O$_2^-$ flows spontaneously from the cathode to the anode. The galvanostat was thus used only to control the current at fixed values. We found that when the anode potential is made positive with respect to the cathode, this has a detrimental effect on product selectivity.

Appropriate setting of two on-off valves (Fig. 1) allows the system to be operated either as a batch recycle reactor or as a continuous-flow steady-state recycle reactor.

We have operated the YSZ SOFC reactor in the batch mode with electrochemical oxygen addition, and the quartz plug flow reactor in the continuous-flow steady-state mode. In the case of continuous flow operation, the molecular sieve trap comprised two packed bed units in parallel in a swing-bed arrangement (Fig. 1), that is, one unit was maintained at low temperature (<70°C) to continuously trap the reactor products while the other was heated for ~30 min to 300°C to release the products in a slow stream of He.

On line G.C. analysis was used to measure product selectivity and methane conversion. Details on the analysis procedure used for batch and continuous-flow operation are given elsewhere (12). The molecular sieve trap was found to trap practically all ethylene, CO$_2$ and H$_2$O produced; a significant percentage of ethane; and practically no methane, oxygen or CO.

RESULTS AND DISCUSSION

Figs. 2 and 3 show typical results obtained with the electrocatalytic YSZ recycle reactor operated in the batch mode. The initial CH$_4$ partial pressure was 20 kPa, i.e. 20% CH$_4$ in He at atmospheric pressure. The recirculation flowrate was 220 cm$^3$/min. Oxygen is supplied electrochemically, at a rate I/2F, through the solid electrolyte walls of the YSZ tube. Figures 2a and 2b show the effect of CH$_4$ conversion and current on the total C$_2$ selectivity and yield and on the C$_2$H$_4$ selectivity and yield, respectively. For any fixed methane conversion, decreasing current, i.e. oxygen supply, causes a pronounced increase in C$_2$ selectivity and yield (Fig. 2a) and also in C$_2$H$_4$ selectivity and yield (Fig. 2b).

As shown in Fig. 2a for $I=5$A and 97% CH$_4$ conversion, the C$_2$ selectivity is 91%, corresponding to a C$_2$ yield of 88%, which is the highest C$_2$ yield obtained so far for the OCM reaction. More importantly under these conditions 97% of the C$_2$ hydrocarbon products is ethylene (Fig. 2b), i.e. the ethylene selectivity is 88% and the ethylene yield is 85%.

Figure 3 shows in detail the effect of CH$_4$ conversion for $I=5$ mA on the C$_2$, C$_2$H$_4$, C$_2$H$_6$ selectivity and yield. The ethylene selectivity can increase with increasing methane conversion because of the predominantly consecutive nature of the OCM reaction network:

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The molecular sieve adsorbent traps ethylene quantitatively, thus practically freezing step 4. Ethane trapping is only partial, thus the desired step 3 is not decelerated significantly. Steps 1, 3 and 4 are predominantly catalytic (or electrocatalytic, depending on the mode of oxygen addition) whereas step 2 is predominantly homogeneous, as established by Lunsford (4).

The observed dependence of $S_{C_2}$, $S_{C_2H_4}$, $S_{C_2H_6}$, $Y_{C_2}$, $Y_{C_2H_4}$ and $Y_{C_2H_6}$ on methane conversion shown in Fig. 3 can be rationalized easily on the basis of the above consecutive reaction network.

In a separate set of experiments oxygen was introduced to the gas phase at a rate comparable to $I/2F$, instead of electrochemically. As shown in Fig. 4 both modes of oxygen addition give practically the same results. This is due to the complete oxygen conversion, since in a recent study we have found that, at moderate oxygen conversion levels in a single pass reactor, electrochemically supplied oxygen can be more active and selective than gas phase oxygen (9). Substituting Ag with a $\text{Sm}_2\text{O}_3$-$\text{CaO}$-Ag cermet gave practically the same results (12).

Figure 5 shows the effect of gas recirculation flowrate on the $C_2$ selectivity and yield at fixed batch operation time. Decreasing the recirculation flowrate from 220 to 30 cc STP/min does not affect significantly the reactor performance. By further decreasing the recirculation flowrate there is a significant loss in $C_2$ selectivity and yield due to the increasing $\text{CH}_4$ conversion per pass.

The improvement in $C_2$ selectivity and yield of the present work, for both batch and continuous flow steady-state operation, is not attributable to the properties of the Ag-based anode which gives yields per pass less than 3%, but is a result of the reactor design. The pronounced enhancement in ethylene yield is a result of the trapping material properties and of the consecutive nature of the OCM reaction network.

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Fig. 1: Schematic of the gas recycle electrocatalytic SOFC or catalytic reactor separator; WE, CE and RE are the working, counter and reference electrodes respectively; PCV: product collection vessel.
Fig. 2: Effect of methane conversion and applied current on the C₂ hydrocarbon (a) and on the ethylene (b) selectivity (filled symbols) and yield (open symbols).
Fig. 3: Effect of methane conversion for I=5 mA on ethylene, ethane and total C₂ hydrocarbon selectivity and yield.

Fig. 4: Comparison of the effect of oxygen supplied electrochemically and from the gas phase on the C₂ selectivity and yield.
Fig. 5: Effect of recirculation flowrate on methane conversion, C₂ hydrocarbon selectivity and yield for constant operation time (30 min); I=7 mA.