Ethylene Production from Methane in a Gas Recycle Electrocatalytic Reactor Separator

I. V. Yentekakis, Y. Jiang, M. Makri and C. G. Vayenas

Department of Chemical Engineering, University of Patras

Patras, GR 26500, Greece

Abstract. It was found that methane can be oxidatively coupled to ethylene with an ethylene yield up to 85% and a total C_2 hydrocarbon yield up to 88%, in a novel gas-recycle electrocatalytic reactor-separator where the recycled gas passes continuously through a molecular sieve trap in the recycle loop. The molecular sieve traps and thus protects a controllable percentage of ethylene and ethane produced during each gas cycle. These products are obtained by subsequent heating of the trap. In this way we have obtained, using the batch operating mode of the recycle reactor, ethylene yields up to 85%, i.e. 88% selectivity to ethylene at 97% CH_4 conversion.

Oxygen is supplied electrochemically to the Ag-Sm_2O_3 or Ag anode via a solid electrolyte, i.e. Y_2O_3-stabilized-ZrO_2, which is a O^{2-} conductor. The cathode is exposed to ambient air and the electrocatalytic reactor operates at 750-830 °C.

1. Introduction

Over the past decade considerable effort has been devoted to the development of processes for the conversion of methane to more valuable chemicals and fuels. Although most efforts have been focused to indirect processes, which involve the formation of synthesis gas (CO and H_2) as the initial step, economic reasons [1] would favor a viable industrial process for the one-step (direct) production of dimerization products.

Keller and Bhasin were first to report in 1982 [2] on the catalytic one-step oxidative dimerization or "coupling" of methane (OCM) to C_2 hydrocarbons, ethane and ethylene. Numerous investigations have followed this seminal work and a large number of catalysts have been found which give selectivities to C_2 hydrocarbons higher than 90% at low (<2%) methane conversion.

However, it was universally found that the total C_2 hydrocarbon selectivity decreases drastically with increasing conversion of methane, so that Y_{C_2} (the total C_2 hydrocarbon yield) was always found, until very recently, to be less than 30% [3-7]. Achieving C_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_2 selectivity values at high

methane conversion C_{CH_4} and thus the reason for the low measured Y_{C_2} and $Y_{C_2H_4}$ yield values of earlier studies is that the desired products, ethylene and ethane, are far more reactive with oxygen than methane and therefore are easily oxidized to CO/CO_2 when their concentrations become comparable to that of methane, i.e. for high methane conversion. Aris and coworkers [8] recently showed that and can be increased up to 50% and 17%, respectively, by using a Sm_2O_3 catalyst in a simulated countercurrent moving bed chromatographic reactor (SCMBCR) to carry out the OCM reaction. The observed significant improvement in C_2 yield (~ 50%) in the case of the SCMBCR is due to the partial separation and removal of C_2 hydrocarbons from unreacted methane and oxygen. Despite the reactor complexity, which may not be easy to adapt to industrial practice [9], this pioneering work created a great deal of interest [9].

We have now found a means to almost entirely eliminate the problem of the high reactivity of the C_2 hydrocarbons during the OCM reaction by using a gas recycle catalytic or electrocatalytic reactor 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
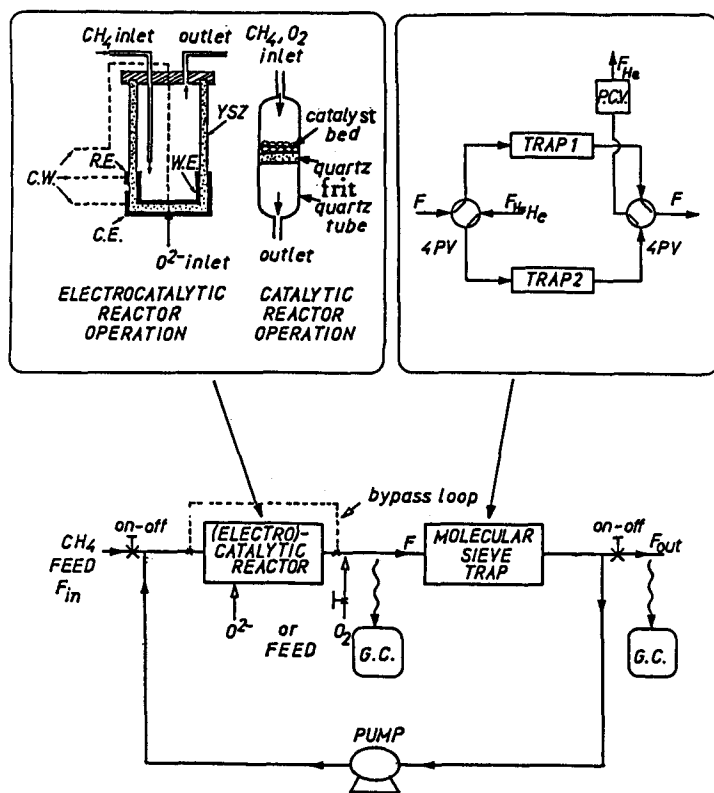
Fig. 1. Schematic of the gas recycle electrocatalytic or catalytic reactor separator; WE, CE and RE are the working, counter and reference electrodes respectively; PCV: product collection vessel.

each gas cycle [10]. 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 [11].

2. Experimental

The gas-recycle reactor, consisting basically of an electrocatalytic reactor unit with a bypass loop, a recycle pump and a molecular sieve trap unit, is shown schematically in Fig. 1. The trap unit comprises one or two packed bed columns in parallel each containing 2-10 g of Linde 5A molecular sieve pellets. The cell reactor consisted of an Y_2O_3 (8mol%)-stabilized ZrO_2 (YSZ) tube (length 15 cm, ID 16 mm) 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]. This type of reactor has been shown to behave as a CSTR [12]. The catalyst electrode was a porous Ag or Ag-Sm_2O_3 film

(mass, 150 mg; superficial area, 10 cm^2) coated on the inside walls of the O^{2-}-conducting YSZ tube (Fig. 1).

The reactor can be operated catalytically or electrocatalytically, depending on the mode of oxygen addition: Oxygen can be supplied either electrochemically by means of the solid electrolyte wall of the reactor (electrocatalytic operation) or in the gas phase (catalytic operation) (Fig. 1). In the case of electrocatalytic operation, a galvanostat is used to apply constant currents I between the catalyst and a Ag 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. In this case the catalyst acts as an electrocatalyst [7,10,12, 13].

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 reactor properly in the batch mode with both electrochemical and gas phase oxygen addition. Some preliminary continuous-flow steady-state experiments were also carried out with electrochemical oxygen addition. 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 gas chromatography was used to measure product selectivity and methane conversion. Details on the analysis procedure used for batch and continuous-flow operation are given elsewhere [10].

3. Results and Discussion

The molecular sieve trap was found to trap practically all (~100%) ethylene, CO_2 and H_2O produced; a significant controllable percentage of ethane (controlled via the adsorbent mass load used in the molecular sieve trap unit); and practically no methane, oxygen or CO, for temperatures 50-70 °C. The trap was heated to ~ 300 °C in order to release all trapped products into the recirculating gas phase (in the case of batch operation), or in a slow He stream (in the case of continuous flow ope-
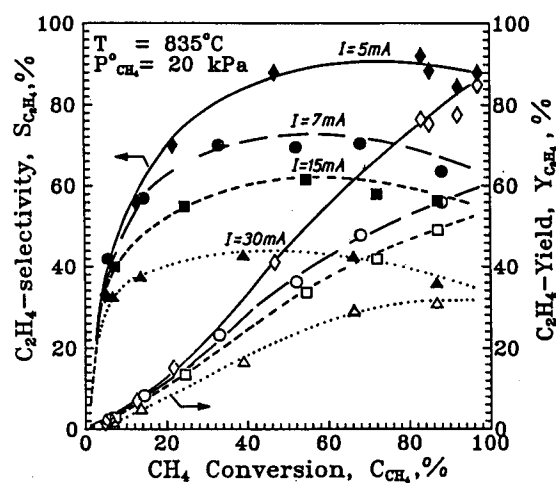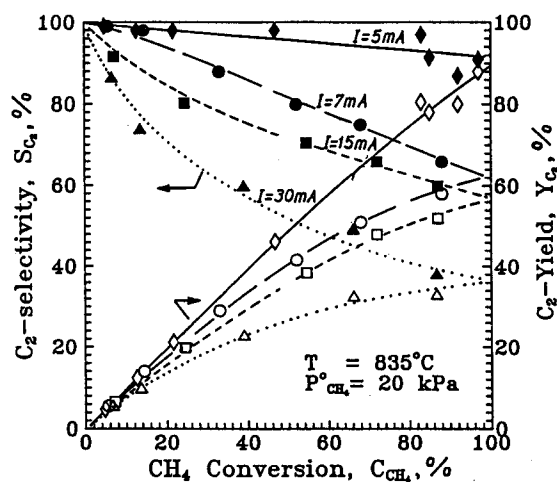
Fig. 2. Effect of methane conversion and applied current on the C_2 hydrocarbon (a) and on the ethylene (b) selectivity (filled symbols) and yield (open symbols).

Fig. 3. Effect of methane conversion for I=5 mA on ethylene, ethane and total C_2 hydrocarbon selectivity and yield.

ration).

Figs. 2a and 2b 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 cm³/min. Oxygen was supplied electrochemically, at a rate I/2F, through the solid electrolyte walls of the YSZ tube. The applied current was always maintained at low levels, so that the catalyst potential V_{WC} with respect to the counter electrode was always maintained negative. Higher currents leading to $V_{WC}{>}0$ were found to lead to poor C_2 selectivity. Consequently all results reported here can be considered as obtained in the chemical cogeneration mode [13], i.e., with spontaneous cell operation. Figure 2 depicts the effect of CH_4 conversion and current on the total C_2 hydrocarbon
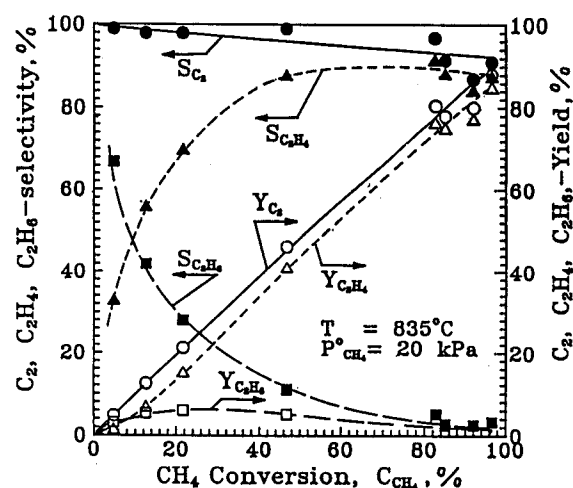
selectivity and yield (Fig. 2a) and on the C_2H_4 selectivity and yield (Fig. 2b). For any fixed methane conversion, decreasing current, i.e. oxygen supply, causes a pronounced increase in C_2 selectivity and yield (Fig. 2a) and also in C_2H_4 selectivity and yield (Fig. 2b).

As shown in Fig. 2a for I=5mA 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%.

The effect of CH_4 conversion on the total C_2, C_2H_4, C_2H_6 hydrocarbon selectivity and yield is shown in detail on Fig. 3 for the case of I=5mA. Interestingly, the ethylene selectivity can increase with increasing methane conversion because of the predominantly consecutive nature of the OCM reaction network:

$$2CH_4 \xrightarrow[1]{O^{2-}} 2CH_3\bullet \xrightarrow[2]{} C_2H_6 \xrightarrow[3]{O^{2-}} C_2H_4 \xrightarrow[4]{O^{2-}} 2CO_2 \qquad (1)$$
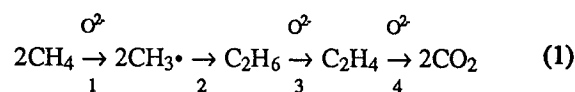
The molecular sieve adsorbent traps ethylene quantitatively, thus practically freezing step 4. Ethane trapping is only partial, thus the desired step 3 is not decelerated significantly. Steps 1,3 and 4 are predominantly catalytic or electrocatalytic, depending on the mode of oxygen addition, whereas step 2 is predominantly homogeneous, as established by Lunsford and co-workers [3,5]. Thus, 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
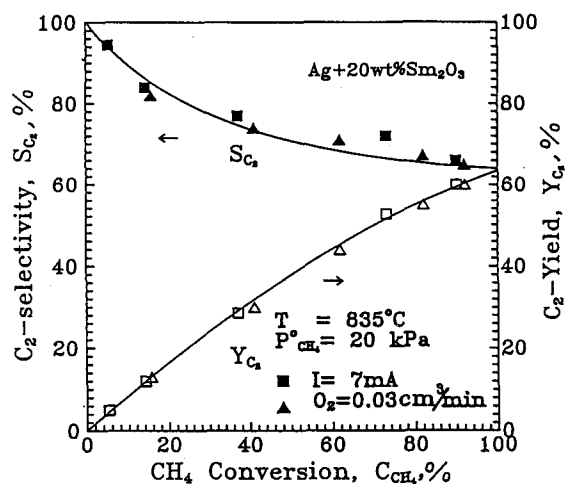
Fig. 4. Comparison of the effect of oxygen supplied electrochemicaly and from the gas phase on the C_2 selectivity and yield.

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 1/2F, 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 [7].

The ethylene selectivity and yield depend strongly (Fig. 5) on the amount of adsorbent for a given mass of catalyst and rate of oxygen supply 1/2F, and for fixed methane conversion, there is an optimal minimum amount of adsorbent for maximizing ethylene selectivity and yield as shown in Fig. 5. Excessive amounts of adsorbent cause quantitative trapping of ethane and thus a decrease in ethylene yield according to the above reaction network.

The YSZ reactor with electrochemical oxygen feed has been also operated in the continuous-flow steady-state mode. Some preliminary results depicting the effect of methane conversion on the total C_2 hydrocarbon selectivity (filled stars) and yield (open stars) are shown in Figure 6. The figure also depicts continuous-flow steady-state results, obtained recently in a quartz plug flow chemical reactor (length 5cm, diameter 1cm) with a fixed catalyst bed of Sr(1wt%)/La_2O_3 pellets (0.5-1 mm diameter, total mass 0.5g). These experiments were carried out at significantly higher flowrates of CH_4 feed, as a
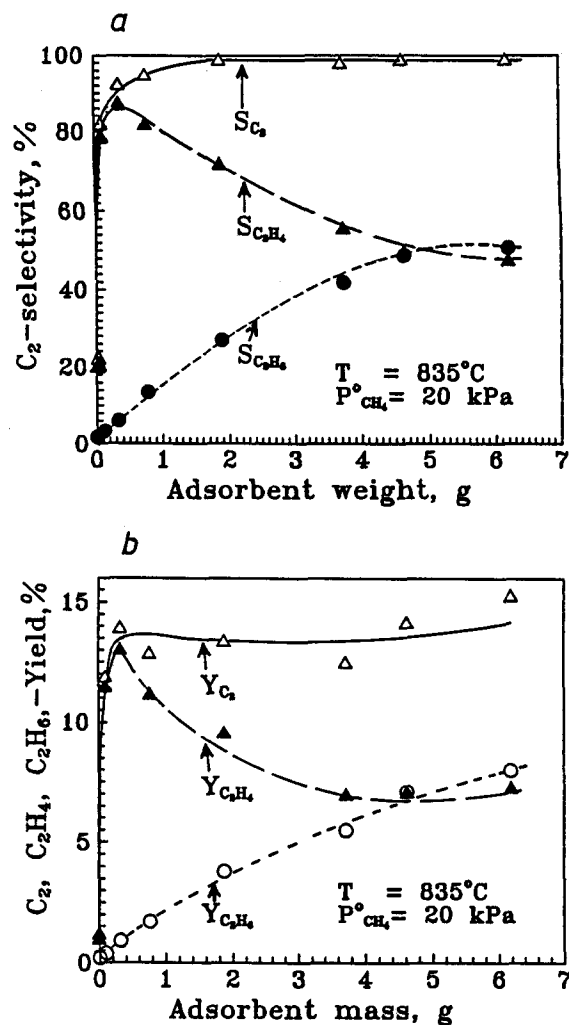

Fig. 5. Effect of adsorbent mass in the molecular sieve trap on ethylene, ethane and C_2 hydrocarbon selectivity (a) and yield (b) at fixed methane conversion C_{CH_4} =15%; T = 835°C; I=7 mA; recirculation flowrate 220 cm^3 STP/min.

first step in the scale-up of the novel recycle reactor separator. The inlet CH_4 partial pressure was 20 kPa (20% CH_4 in He) at inlet flowrate of 7.1 cm^3 STP/min, while a 20% O_2 in He mixture was supplied directly, at a flowrate F_{O_2}, in the recycle loop via a needle valve placed after the reactor (Fig. 1). The methane conversion was controlled by adjusting F_{O_2}, which was kept at appropriately low levels so that the oxygen conversion was always higher than 95%. In this way the oxygen partial pressure in the recycle loop is very low and thus no explosive mixtures with CH_4 can form. Figure 6a shows the effect of CH_4 conversion on the selectivity and yield of ethylene, ethane and total C_2 hydrocarbons. Figure 6b refers to the same experiments and shows the corresponding effect of F_{O_2} on the C_2 selectivity and yield.
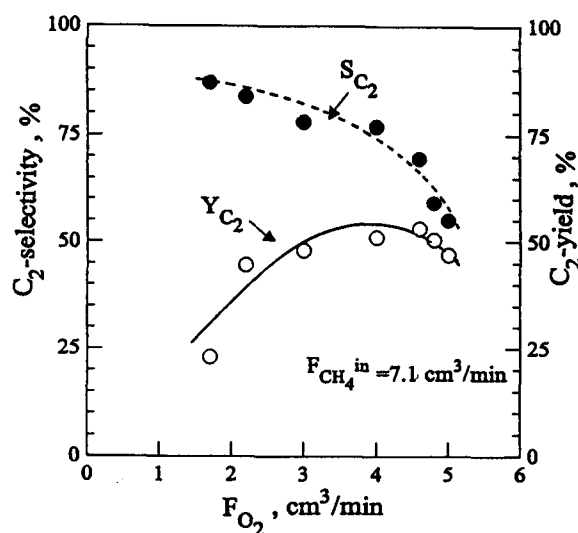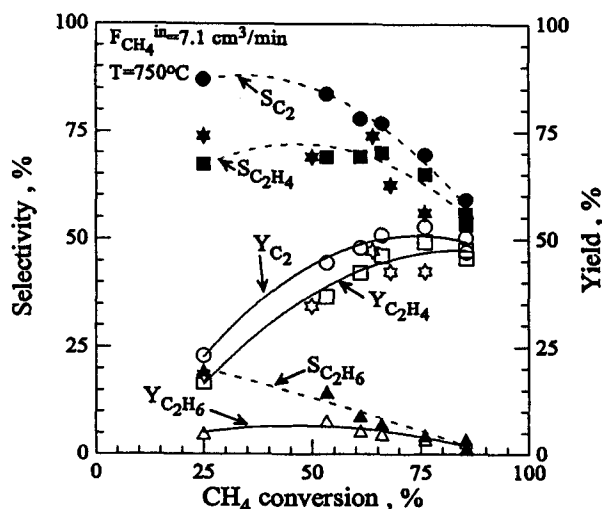
Fig. 7. Fuel cell operation: Effect of current on cell voltage VCW and power output during the OCM reaction on a Ag+20wt% Sm_2O_3 (1%CaO) electrocatalyst with single pass operation; inlet partial pressure of CH_4 = 11 kPa (11% CH4 in He and atmospheric pressure); T=835°C; C_2 hydrocarbon selectivity >95%; CH_4 conversion <0.5%; inlet flowrate 20 cm^3 STP/min.

Fig. 6. Continuous flow steady-state operation: (a) Effect of methane conversion on the selectivity and yield of C_2H_4, C_2H_6 and total C_2 hydrocarbons. In the case of the YSZ electrochemical reactor unit (stars; see text for discussion) the experiments were performed at I=30, 5, 5, 7 and 9 mA and outlet volumetric flowrate F_{out} = 3, 0.3, 0.2, 0.3, and 0.3 cm^3STP/min respectively, for the five points shown in the order of increasing CH_4 conversion; recirculation flowrate 220 cm^3STP/min; Ag catalyst; T=835°C. In the case of the plug flow catalytic reactor unit the catalyst is Sr/La_2O_3 with T=750°C and a recirculation flowrate of 200 cm^3 STP/min; (b) corresponding effect of oxygen stream flowrate on C_2 selectivity and yield.

The C_2 yield is up to 53% while the ethylene yield is up to 50% (65% ethylene selectivity at 76% methane conversion). To the best of our knowledge this is the maximum ethylene yield obtained for the OCM reaction under continuous-flow steady-state conditions.
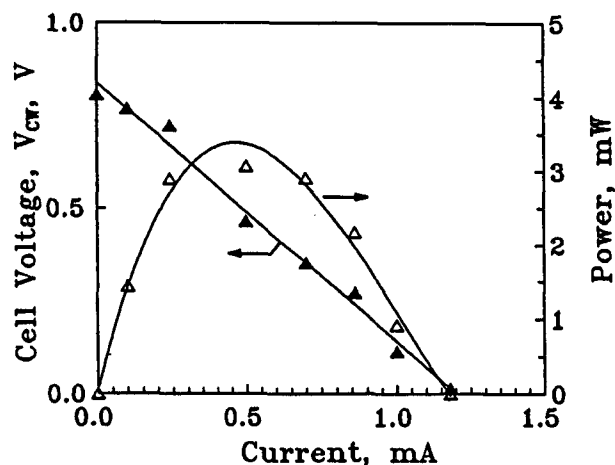
Figure 7 shows the dependence of the YSZ electrochemical cell-reactor voltage V_{CW} (C and W stand for the counter and working electrode respectively) on the spontaneously generated current, during the OCM reaction under single pass conditions, i.e., without gas recycle. The inlet stream CH_4 partial pressure was 11 kPa (11% CH_4 in He at atmospheric pressure) and the flowrate was 20 cm^3 STP/min. Oxygen was spontaneously pumped from ambient air through the YSZ solid electrolyte walls by means of the Ag cathodic electrode, with a rate of 1/2F mol O/s. The electrocatalyst was a Ag + 20% Sm_2O_3(1%CaO) cermet film. A decade resistance box was used to vary cell load and thus cell potential and current. As shown in Fig. 7 the cell voltage decreases quasilinearly with current indicating the absence of activation and concentration overpotentials. Consequently the ohmic resistance of the solid electrolyte and the electrodes are the main sources of cell polarization. Due to the significant thickness (2 mm) of the solid electrolyte, the measured electrical power density production of the cell is low, but the results show the possibility of using the OCM reaction for chemical cogeneration [13] i.e., simultaneous production of valuable products and electrical power.
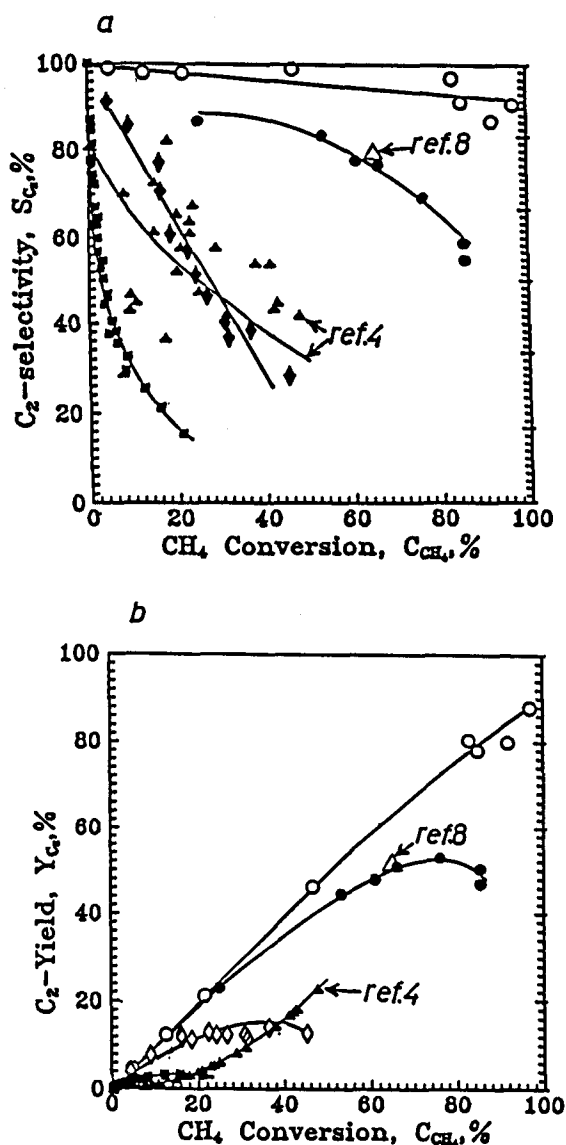
Fig. 8. Effect of methane conversion on C_2 selectivity (a) and C_2 yield (b) for some of the best state-of-the-art OCM catalysts (closed triangles, based on ref. 4), the simulated chromatographic reactor of Aris and coworkers (open triangle, ref. 8) and the present work without (filled rhombi and squares) and with (filled and open circles) gas recycling and C_2 trapping. Open symbols, batch operation; filled symbols, continuous-flow steady-state operation.

We compared the highest literature C_2 selectivity and yield values on the basis of Fig. 8 of the review article of Lee and Oyama [4], the pioneering work of Aris and coworkers [8], the present results of the novel gas recycle reactor, and the results obtained under the same operating conditions but without gas recycling and molecular sieve trapping (single pass conditions). It is clear that the very significant 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 catalyst used, particularly for the case of Ag catalyst which is in fact inferior to most state-of-the-art catalysts and gives yields per pass less than 3%, but is a result of the present reactor design. It is also clear from Fig. 8 that batch or periodic batch (unsteady-state) reactor operation gives higher performance than steady-state reactor operation, although industrial practice favors, in general, the latter mode of operation. The pronounced enhancement in ethylene yield for both modes of operation is a result of the trapping material properties and of the consecutive nature of the OCM reaction network.

4. References

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