THE CATALYTIC AND ELECTROCATALYTIC COUPLING OF METHANE OVER YTTRIA-STABILIZED ZIRCONIA

D. ENG and M. STOUKIDES *

Department of Chemical Engineering, Tufts University, Medford, MA 02155, U.S.A.

The catalytic and electrocatalytic oxidation of methane to ethane and ethylene was studied at 900 °C over a gold-supported yttria-stabilized zirconia (Au-YSZ) catalyst. The catalyst was found to be active for C_2 formation with C_2 selectivities up to 67% and C_2 yields up to 15%. Yttria-stabilized zirconia compared favorably to unstabilized yttria-zirconia. Electrochemical oxygen pumping was investigated and found to affect product distribution.

1. Introduction

Recently, there has been considerable interest in the conversion of methane to ethane and ethylene. The oxidative coupling of methane has been reviewed [1] and studied over numerous oxides including Bi_2O_3, PbO, Li/MgO, and Sm_2O_3 [2,3]. It is considered that the coupling reaction proceeds via surface formation of methyl radicals which are subsequently coupled in the gas phase to form ethane [1–3].

In the last decade, there has been increasing research in the applications of oxygen-ion conducting solid electrolytes to heterogeneous catalysis [4–7]. A most promising application is the electrochemical oxygen pump in which a current is applied to the electrolytic cell to pass O^{--} through the electrolyte to the catalyst. This method has been used to electrochemically influence intrinsic catalytic activities and selectivities during methane oxidation [4–7]. In the present work, the catalytic and electrocatalytic oxidation of methane over Au-YSZ is investigated. An objective of this study was to electrocatalytically enhance the rates of formation of C_2 products.

* To whom correspondence should be addressed.

2. Experimental

A schematic diagram of the reactor cell is shown in fig 1. The reactor has been shown to behave similarly to a continuously stirred tank reactor [8]. It consisted of an 8 mol% Y_2O_3-stabilized ZrO_2 (YSZ) tube (16 mm ID, 1.8 mm wall thickness) open at both ends and enclosed in a quartz tube (22 mm ID). The heated volume of the reactor was 7 cm³. Experiments were conducted at 900 °C. Reactants were CH_4 and O_2 gases diluted in He. Products and reactants were analyzed using on-line gas chromatography. Constant current across the cell could be applied using a galvanostat. Cell voltage and current were measured by two digital multimeters.

The cathode was prepared by painting inside the YSZ tube with a Ag-Fe solution which was dried and calcined in air for 2 hours at 650°C. The anode-catalyst was prepared by painting the outer YSZ wall over a 9 cm length with gold phase (Engelhard A3798) which was calcined at 700°C for 4 hours. Either the unstabilized or stabilized yttria-zirconia was applied to the gold electrodic support by depositing a second paste layer of Au and yttria-zirconia powder. Unstabilized Y_2O_3-ZrO_2 (UYZ, 8 : 92 mol) was prepared by mixing powders (Aldrich Chemical) of the two oxides. The YSZ catalyst was prepared by grinding a tube obtained from Zircoa, Inc.

Scanning electron microscopy revealed that the unstabilized Y_2O_3-ZrO_2 had uniform particles averaging 4.3 μm in diameter [8]. The YSZ particles were widely
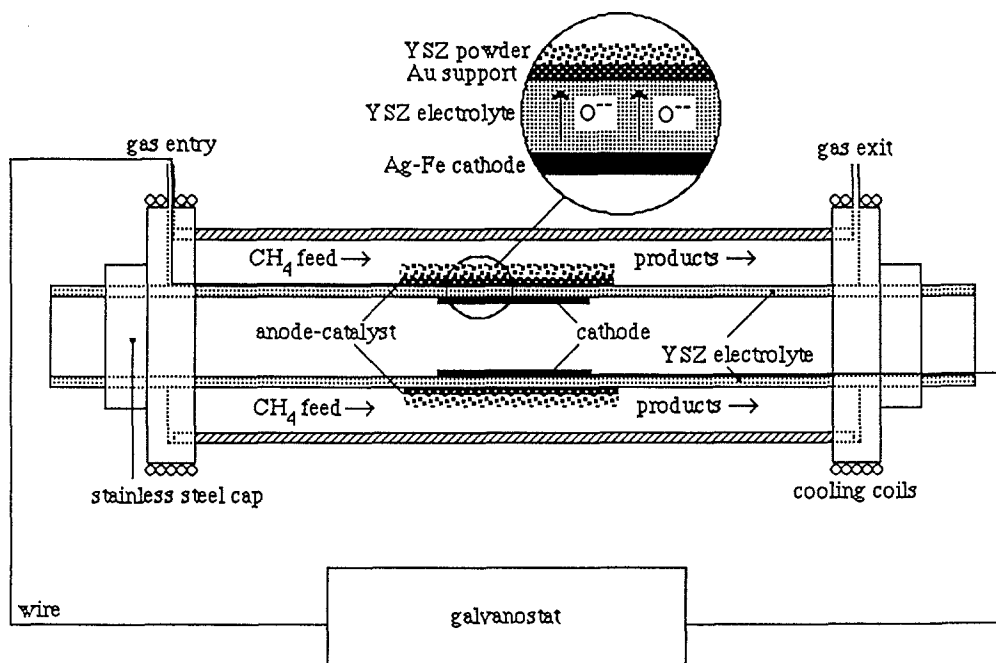

Fig. 1. Schematic diagram of reactor cell and circuit.

irregular in shape averaging 30–40 μm. Different masses were used so that both catalysts had 200–225 cm^2 area when deposited on the Au support.

3. Results

The reaction over gold and the non-catalytic reaction were studied first [8]. Barring explosive compositions [8], the homogeneous reaction rate was < 3% of the rates obtained with Au-YSZ.

The effect of flow rate on C_2 selectivity ($C_2H_6 + C_2H_4$) and C_2 yield over Au-YSZ is shown in fig. 2. As flow rate increases, selectivity increases but yield decreases. Furthermore, the C_2H_4/C_2H_6 product ratio increases upon decreasing flow rate. Both observations are expected since the sequence of products is $CH_4 \rightarrow C_2H_6(+CO_x) \rightarrow C_2H_4 \rightarrow CO_x$ [1]. In subsequent figures, moderate flow rates (250–425 cc/min) were used to reduce the effect of residence time.
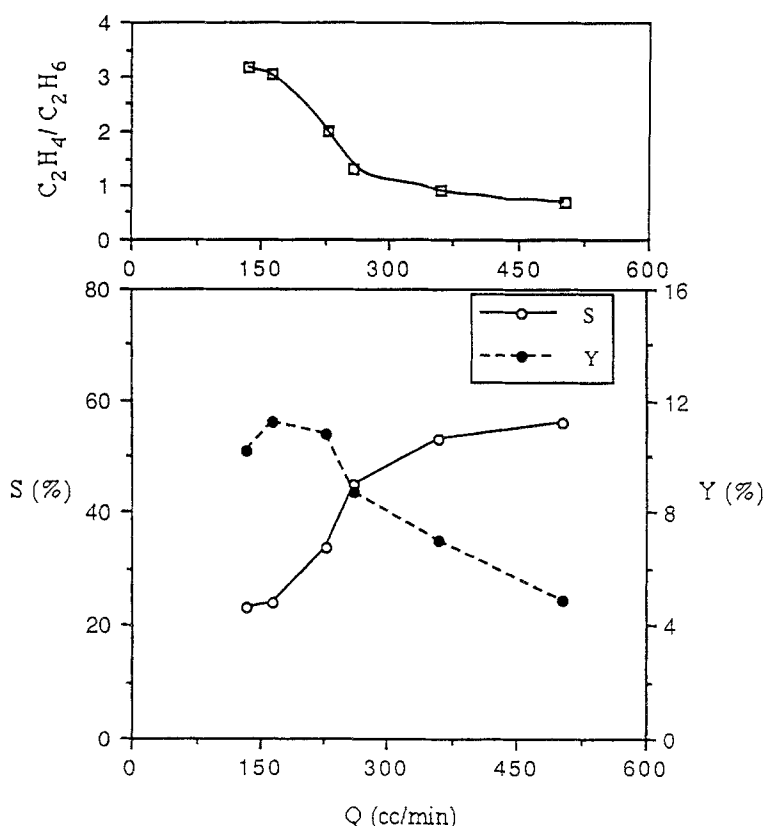

Fig. 2. Effect of flow rate on C_2H_4/C_2H_6 product ratio, selectivity and yield. $T = 900\,^\circ$C, $P_{CH_4,outlet} = 0.066$ bar, $P_{O_2,outlet} = 0.24$ bar.
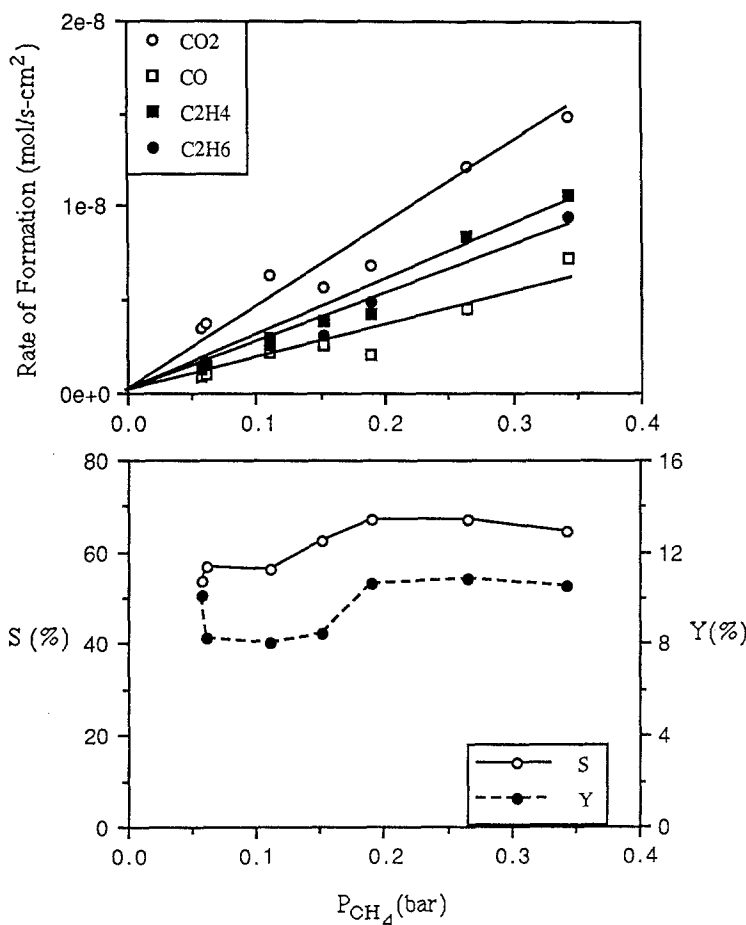
Fig. 3. Effect of $P_{CH_4,outlet}$ on rates of formation, C_2 selectivity, and C_2 yield. $T = 900\,°C$, YSZ catalyst area = 225 cm^2.

In figs. 3 and 4, the rates of product formation, C_2 selectivities, and C_2 yields vs. $P_{O_2,outlet}$ and $P_{CH_4,outlet}$ are shown. The catalyst loading was 0.94 g YSZ (Au:YSZ = 1:4). In fig. 3, maximum selectivity reached 67.3% and the yield reached 10.8%. In separate experiments, at flow rates under 250 cc/min and larger catalysts loading (3.4 g YSZ, Au:YSZ = 1:4), the yield reached 15.4% with C_2 selectivity at 51.4% [8]. In fig 4, increasing P_{O_2} increased yield but decreased C_2 selectively. A power law rate expression for total methane consumption was derived; i.e., $r = k\ P_{CH_4}^{1.0}\ P_{O_2}^{0.35}$.

A comparison of the catalytic activities of YSZ and UYZ is shown in fig. 5 where methane reaction rates were of the same order (10^{-6} mol/s). Identical flow rates (≈ 425 cc/min) were used for both catalysts. The Au-UYZ catalyst appears to be much less selective than Au-YSZ. Upon increasing P_{CH_4}, the CO/CO_2 and C_2H_4/C_2H_6 ratios increase for YSZ but not for UYZ. In addition, YSZ was found not to lose catalytic activity over 180 continuous hours of experiments.
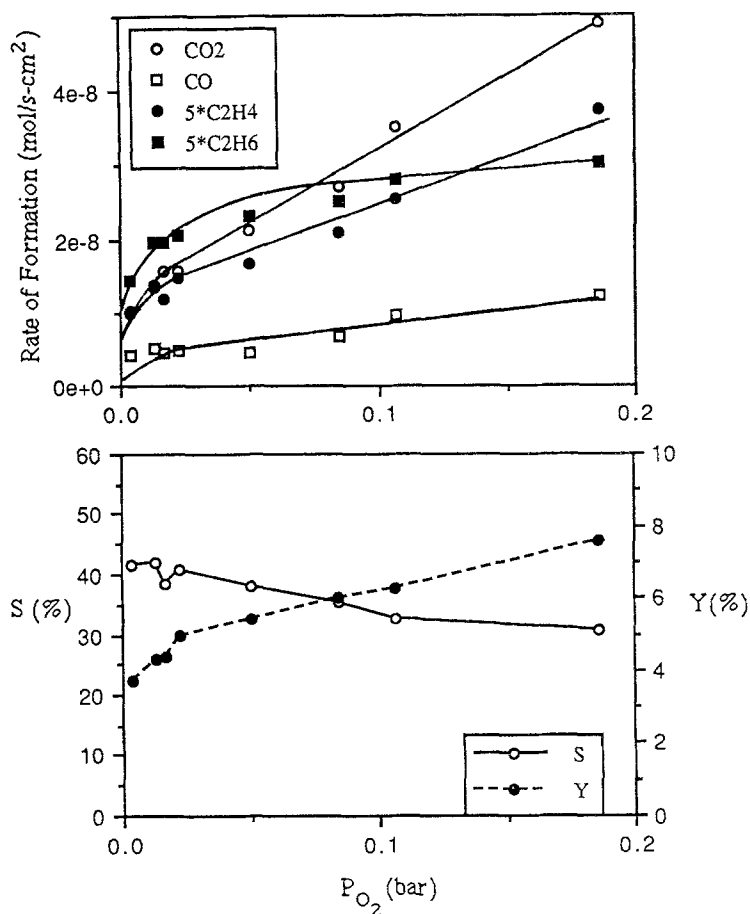
Fig. 4. Effect of $P_{O_2,outlet}$ on rates of formation, C_2 selectivity, and C_2 yield, $T = 900\,^\circ C$, YSZ catalyst area $= 225$ cm^2.

It is possible that methane could be activated by O^{--} sites on the YSZ catalyst in which case, YSZ may exhibit electrocatalytic behavior. Hence, electrochemical oxygen pumping (EOP) was investigated with the Au-YSZ electrode and results are shown in fig. 6. The terms r and r_0 represent the rates of formation with and without pumping, respectively. Hence, r/r_0 is the normalized change in rate. The rate enhancement factor Λ is defined from $\Lambda = (r_{O_2}\text{-}r_{O_2,0})/(i/4F)$ [9] where r_{O_2} and $r_{O_2,0}$ are the rates of oxygen consumption with and without pumping and F is the Faraday constant. The current i is taken as positive ($+$) if O^{--} is pumped to the Au-YSZ catalyst. EOP affected CO and CO_2 formation more than C_2 formation. Hence, selectivity slightly decreases with increasing current but yield improves marginally. Results were very similar with other CH_4 and O_2 compositions. In the absence of gas feed oxygen, the principle product upon pumping was CO. Similar results were noted for EOP over only gold support. The rate enhancement factor was near unity upon pumping to the Au-YSZ catalyst which
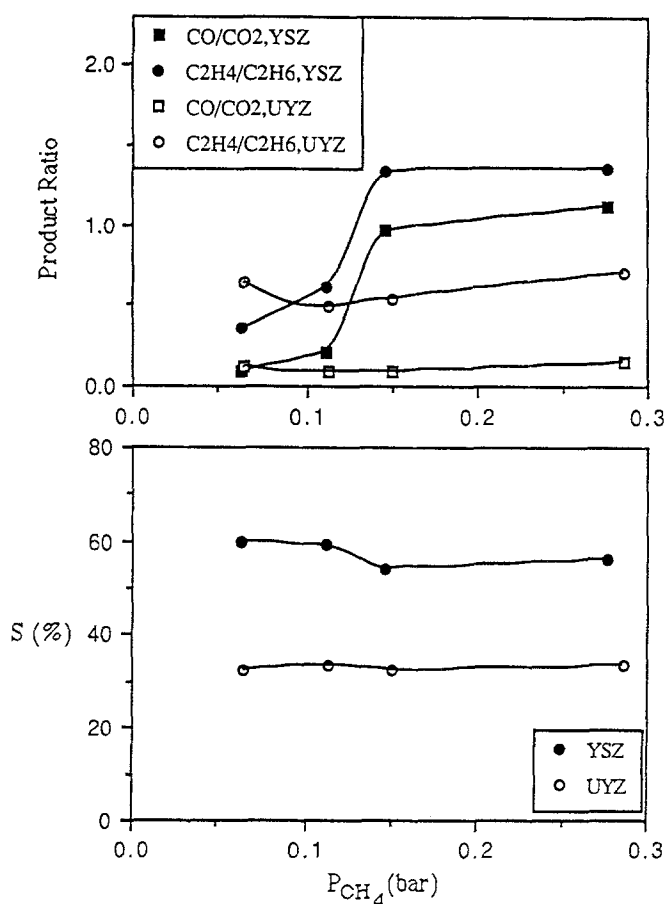
Fig. 5. Comparison of stabilized and unstabilized Y_2O_3-ZrO_2 showing ratios of products and C_2 selectivity. $T = 900\,°C$, $P_{O_2} = 0.032$ bar, $Q \approx 424$ cc/min.

is considerably lower than other oxidation studies where $\Lambda = 10^2$–10^5 but is close to those values obtained for methane oxidation over Ag and Pt [4,5].

4. Discussion

Gold is considered a poor methane oxidation catalyst [10] and thus has been used as an electrocatalytic support [6,10]. It is possible that CO_x was largely affected during EOP because most of the electrochemically supplied oxygen was confined to the gold phase rather than YSZ powder which is a poor electronic conductor. This phenomenon appears to be very much similar to that observed over Ag-Bi_2O_3 [7] where it was suggested that pumped oxygen reacted on Ag to lower selectivity.
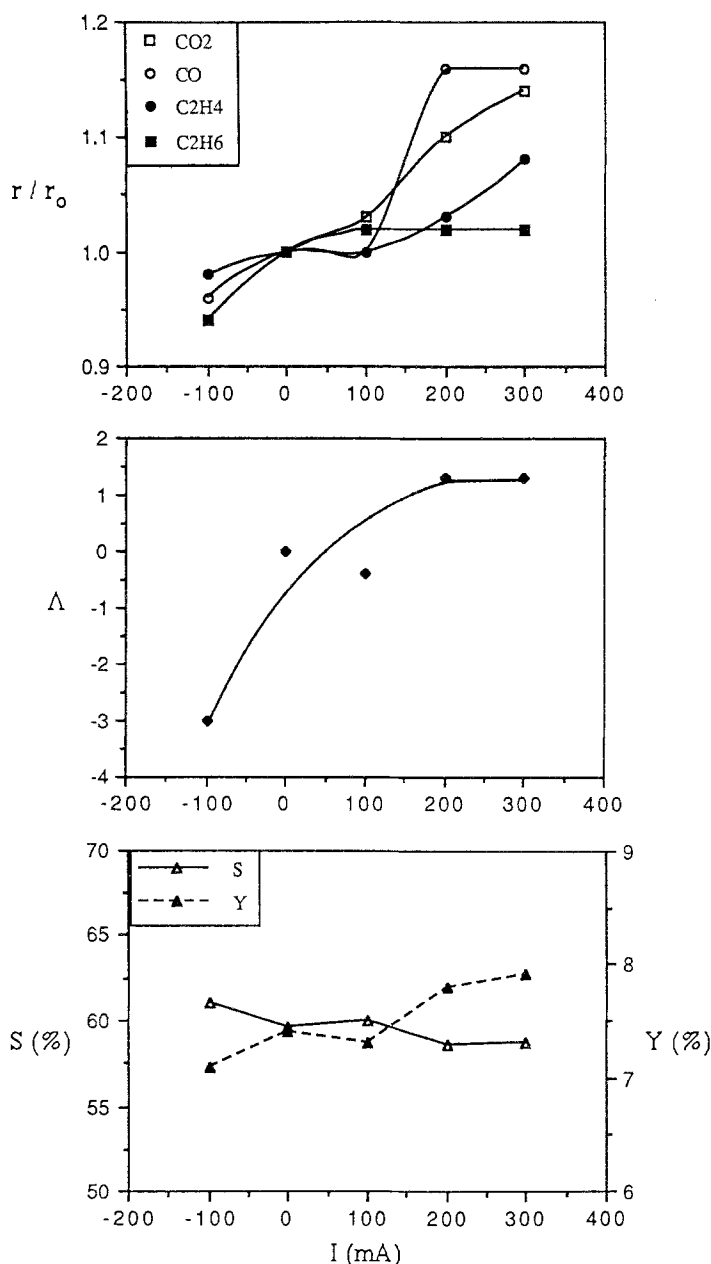
Fig. 6. Effect of electrochemical oxygen pumping on r/r_0, Λ, C_2 selectivity, and C_2 yield. $T = 900\,^\circ C$, $P_{O_2} = 0.0024$ bar, $P_{CH_4} = 0.26$ bar at $i = 0$.

It has been reported that yttria itself is active for C_2 formation [2], however, doping of ZrO_2 with Y_2O_3 may enhance sites active for methane activation. It has been suggested that oxygen vacancies in YSZ may be important for synthesis gas reactions [11]. The oxygen vacancy is reportedly adjacent to Zr^{4+} sites rather

than Y^{3+} [12]. Doping to produce stable oxide catalysts only recently have been investigated since most active catalysts such as Li/MgO deactivate easily [13]. In Ba-doped CaO, the suggested active oxygen species is O_2^{2-} [13]. Although the oxygen vacancy is YSZ is O^{2-}, no speculations about the active oxygen species in the lattice or on the surface can be made at this time.

Although large rate enhancements were not achieved as with other reactions [4,5], EOP can affect C_2 selectivity and formation. A possible explanation for the small electrocatalytic effect is that the mechanism of methane coupling involves both surface and gas-phase steps. Oxygen pumping–which can only modify the surface–cannot affect methane coupling to the same degree as with a purely heterogeneous catalytic reaction.

A major advantage of the YSZ catalyst, compared to most other oxides, is that YSZ is highly stable to over $1000\,^{\circ}C$ and is difficult to reduce. In addition, ceramic YSZ does not change morphology nor specific surface area easily. YSZ has a much longer catalytic life than more selective C_2 catalysts.

References

[1] J.S. Lee and S.T. Oyama, Catal. Rev.-Sci. Eng. 30 (1988) 249.
[2] K. Otsuka, K. Jinno and A. Morikawa, J. Catal. 100 (1986) 353.
[3] T. Ito and J.H. Lunsford, Nature (London) 314 (1985) 721.
[4] C.G. Vayenas, S. Bebelis and S. Ladas, Nature (London) 343 (1990) 625.
[5] C.G. Vayenas, S. Bebelis, I.V. Yentekakis, P. Tsiakaras and H. Karasali, Plat. Metals Rev. 34 (3) (1990) 122.
[6] K. Otsuka, K. Suga and I. Yamanaka, Catal Lett. 1 (1988) 423.
[7] K. Otsuka, S. Yokoyama and A. Morikawa, Chem. Lett. (1985) 319.
[8] D. Eng, Ph.D. Thesis, Tufts University, 1990.
[9] C.G. Vayenas, S. Bebelis and S. Neophytides, J. Phys. Chem. 92 (1988) 5083.
[10] S. Seimanides, Ph.D. Thesis, Tufts University, 1987.
[11] N.B. Jackson and J.G. Ekerdt, J. Catal. 126 (1990) 31.
[12] C.R.A. Catlow, A.V. Chadwick, G.N. Greaves and L.M. Moroney, J. Am. Ceram. Soc. 69 (1986) 272.
[14] S.J. Korf, J.A. Roos, J.W.H.C. Derksen, J.A. Vreeman, J.G. Van Ommen and J.R.H. Ross, App. Catal. 59 (1990) 291.