JOURNAL OF CATALYSIS **130**, 306–309 (1991)

NOTES

Catalytic and Electrochemical Oxidation of Methane on Platinum

The partial oxidation of methane to ethane and ethylene is of considerable interest and has been recently reviewed (*1*). It is widely accepted that over selective catalysts, including Li/MgO, Bi_2O_3, and Sm_2O_3 (*2, 3*), methane initially reacts on active sites to form $CH_3\cdot$ radicals which combine in the gas phase to form C_2H_6.

Several investigators have recently used solid electrolyte reactor cells to influence the intrinsic catalytic activity or product selectivity (*4–9*). In this work, the catalytic and electrocatalytic oxidation of methane over Pt is investigated in a solid electrolyte cell to find if C_2 formation can be electrocatalytically enhanced. To aid kinetic understanding, solid electrolyte potentiometry (SEP) is used to measure the thermodynamic activity of adsorbed oxygen.

The reactor chamber is schematically shown in Fig. 1 (*7*). The fuel chamber was formed between a quartz tube (22 mm i.d.) and a 8% Y_2O_3-stabilized ZrO_2 (YSZ) tube (16 mm i.d., 1.8 mm wall thickness). The heated volume of the reactor was 7 cm^3. Reactants were pure or diluted CH_4 and O_2 in He. Products and reactants were analyzed using on-line gas chromatography. It has been shown that the dynamic behavior of the reactor was very similar to that of a CSTR (*7*).

Outside the YSZ tube, the Pt (Pt ink, Engelhard A4338) anode-catalyst was painted over 9–10 cm, dried, and pretreated in air at 900°C for 24 h. Inside the zirconia tube, the Pt cathode was applied similarly. The average platinum crystallite size was about 5 μm. The superficial catalyst surface area was 55 cm^2 and the active catalytic area was about 500 cm^2. Thin-gauge Pt wires connected the anode and cathode to a voltmeter or galvanostat.

The basic principle of solid electrolyte potentiometry (SEP) has been described previously (*8*). If certain conditions are met (*8*), the open-circuit cell emf E, gives the thermodynamic activity of atomic oxygen, a_O, adsorbed on the catalyst surface by

$$a_O = (0.21)^{1/2} \exp(2FE/RT), \qquad (1)$$

where 0.21 is the mole fraction of O_2 in air. If the catalytic reaction is limited by adsorption of oxygen, gaseous and adsorbed oxygen are not in equilibrium, i.e., $a_O^2 \ll P_{O_2}$. For no reaction, equilibrium exists between adsorbed and gaseous oxygen, i.e., $a_O^2 = P_{O_2}$.

The kinetics of CH_4 oxidation were studied at 600–900°C, $P_{CH_4,\text{outlet}} = 0.027$–$0.49$ bar, $P_{O_2,\text{outlet}} = 0.016$–$0.48$ bar, and 1 atm total pressure. The absence of external diffusion effects was verified by varying the total flow rate at constant gas composition and observing negligible reaction rate change. Surface oxygen activity measurements showed absence of internal diffusion limitations (*7*). Products in the effluent stream were CO_2, H_2O, CO, H_2, C_2H_4, and C_2H_6.

The contribution of homogeneous methane oxidation was investigated by replacing the YSZ tube with a smooth quartz tube without Pt. Reaction rates at 700°C were less than 3% of the corresponding heterogeneous rates. At 900°C, the homogeneous rates could become nearly comparable to heterogeneous rates under oxygen-rich conditions. Homogeneous rates were subtracted from results obtained with Pt.

The reaction was studied at 600–900°C for

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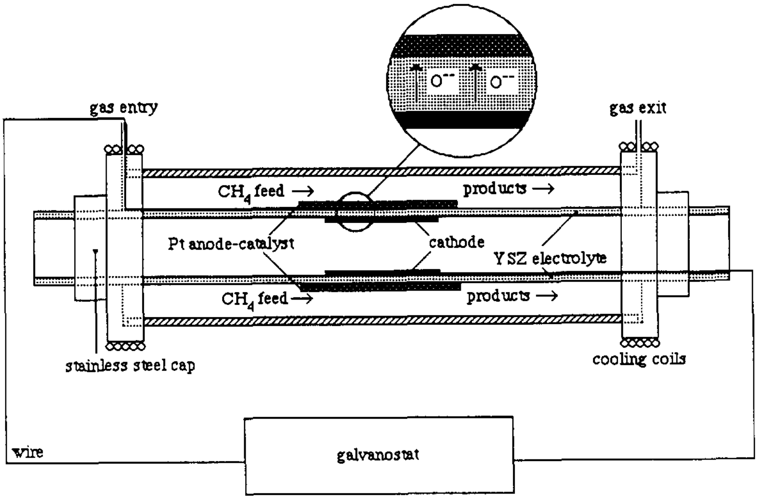

FIG. 1. Schematic diagram of reactor cell and circuit.

constant $P_{CH_4,outlet} = 0.033$ bar and also for constant $P_{O_2,outlet} = 0.033$ bar. At 900°C, C_2 selectivity ($C_2H_4 + C_2H_6$) reached 15% with C_2 yields up to 4%. Figure 2 shows effect of P_{O_2} on a_O, selectivity, and yield at 900°C. At 600–700°C, C_2 formation was negligible. Figure 3a shows that the rates of methane consumption at 600–900°C were well correlated to $P_{CH_4}^{0.80}P_{O_2}^{0.28}$.

Corresponding surface activity data showed that there was a weak decrease in a_O with increasing P_{CH_4} and a moderate increase in a_O with increasing P_{O_2}. It was found that a_O was independent of temperature and only slightly less than $P_{O_2}^{1/2}$ (Fig. 2), in contrast to previous studies where 3–8 orders of magnitude deviation was found between a_O and $P_{O_2}^{1/2}$ (*8*). Figure 3b shows the dimensionless activity deviation $(P_{O_2} - a_O^2)/a_O^2$ linearized to a power law expression, $kP_{CH_4}^{0.5}P_{O_2}^{0.25}$.

Kinetic and potentiometric results were combined to elucidate the reaction mechanism. Assuming dissociative adsorption of oxygen on Pt, the steady-state material balance for adsorbed oxygen is

$$k_aP_{O_2}\theta_m^2 - k_d\theta_O^2 - r_s = 0, \qquad (2)$$

where θ_m, θ_O are the fractional coverages of empty sites and atomic oxygen, respectively, k_a, k_d are adsorption and desorption rate constants, and r_s is the rate of sur-

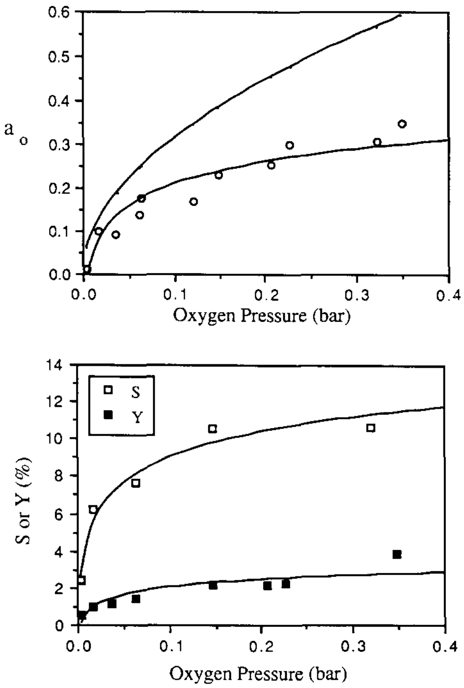

FIG. 2. Effect of P_{O_2} on (a) a_O, and (b) C_2 selectivity, and yield at 900°C for $P_{CH_4} = 0.033$ bar. The top line in (a) represents $a_O = P_{O_2}^{1/2}$.

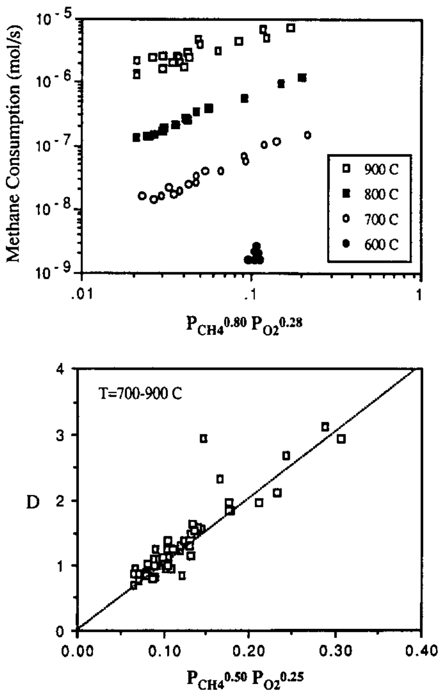

FIG. 3. (a) Plot of reaction rates (mol CH_4 consumed/s) vs $P_{CH_4}^{0.80}P_{O_2}^{0.28}$. (b) Plot of $D = (P_{O_2} - a_O^2)/a_O^2$ vs $P_{CH_4}^{0.5}P_{O_2}^{0.25}$ for 600–900°C. $(P_{O_2} - a_O^2)/a_O^2$ values are independent of temperature.

face oxygen consumption. Substituting $(k_a/k_d)^{1/2}a_O\theta_m$ for θ_O in Eq. (2) (*10*), one gets

$$(P_{O_2} - a_O^2)/a_O^2 = r_s/(k_a\theta_m^2 a_O^2). \quad (3)$$

The left side of Eq. (3) is the dimensionless group plotted in Fig. 3b. Therefore, Eq. (3) can be rewritten as

$$r_s = k\,k_d P_{CH_4}^{0.5}P_{O_2}^{0.25}\,\theta_O^2. \quad (4)$$

The overall reaction rate of methane consumption was proportional to $P_{CH_4}^{0.80}P_{O_2}^{0.28}$ and the homogeneous reaction rate is nearly first order with respect to methane (*7*). Hence, the dependence on methane changes from $\frac{1}{2}$ for the surface reaction, to unity for homogeneous reaction, and the combined total rate is proportional to 0.80 which is between the other two values. From Fig. 3a, an apparent activation energy of 51.5 kcal/mol was calculated for the overall reaction. Equation (4) shows that r_s is proportional to $k\,k_d$ where k is temperature-independent. The temperature dependence of k_d has been reported as 50–55 kcal/mol (*11*). Finally, the homogeneous reaction of CH_4 and O_2 is reported to have an apparent activation energy near 53 kcal/mol (*12*). Clearly, all three reactions have the same apparent activation energy which implies that the rate-determining step for the gas phase and the surface oxygen consumption may be the same, which is the abstraction of hydrogen from CH_4 to form $CH_3\cdot$. The difference in P_{CH_4} dependence can be explained if we consider that in the non-catalytic case, gaseous CH_4 reacts, while in the surface reaction, CH_4 is adsorbed on Pt before its H abstraction occurs and thus its order with respect to P_{CH_4} is lower (*13*).

It is of interest to examine the effect of electrochemical oxygen pumping (EOP) on the rate of surface oxygen consumption and whether C_2 formation could be enhanced during pumping. Figure 4 shows EOP results at 600–800°C for oxygen-rich conditions, i.e., $P_{O_2}/P_{CH_4} = 2.5$. The rate enhancement factor Λ is defined as $\Lambda = (r - r_O)/(i/2F)$ where r, r_O are the rate of atomic oxygen consumption during closed- and open-circuit, respectively, and F is the

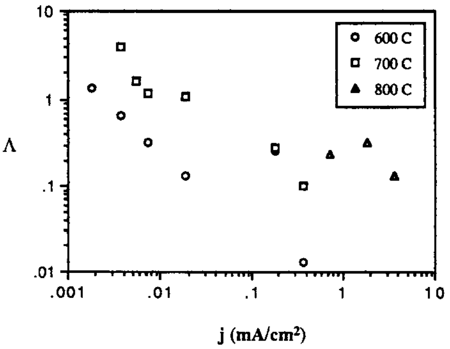

FIG. 4. Effect of current density j on rate enhancement factor Λ for $P_{O_2}/P_{CH_4} \approx 2.5$.

Faraday constant. Only trace C_2's were detected as was the case with open-circuit kinetics. The rate enhancements for $|j| \leq 0.3$ mA/cm^2 were typically 10^{-1}–10^0. At higher current densities, there appears to be no additional effect on r/r_O. When no gas-phase oxygen was fed ($P_{CH_4} = 0.15$ bar, $P_{He} = 0.85$ bar) at 900°C, the consumption of O^{2-} at the anode-catalyst was faradaic; i.e., $\Lambda = 1.0$ or oxygen conversion $\approx$100%, for current densities up to 12.7 mA/cm^2. Selectivities, typically 10–20%, were not significantly different from those at oxygen-rich conditions (Fig. 2b).

The low enhancement factors found in this study appear in general agreement with most recent reports of $\Lambda < 5$ over Pt and Ag which is small compared to other oxidation reactions where $\Lambda = 10^2$–10^5 (*5, 6*). The fact that CO_2 and not C_2's was the main product upon pumping indicates that oxygen pumping on platinum does not increase the number of active sites for coupling. A possible explanation for this weak enhancement is that the reaction of methane coupling involves both surface and gas-phase reaction steps. Electrochemical oxygen pumping can modify surface properties, not gas-phase reactions. Therefore, a surface modification is not expected to enhance a reaction whose critical steps (e.g., $2\ CH_3\cdot \rightarrow C_2H_6$) are widely believed to occur in the gas phase (*1–3*). It is thus reasonable to observe a weaker effect compared to studies where the reaction is entirely catalytic.

ACKNOWLEDGMENTS

We gratefully acknowledge the National Science Foundation for support of this research under Grants CBT-8711870 and CBT-8815927 and the Department of Energy under Grant DE-FG02-89CE90048.

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Received December 20, 1989; revised January 21, 1991

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