Partial oxidation of methane catalyzed by $YBa_2Cu_3O_x$ in a solid state electrochemical reactor

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The catalytic oxidation of methane was studied between 840 and 1110 K on a $YBa_2Cu_3O_x$ mixed-conducting electrode deposited on an yttria stabilized zirconia solid electrolyte. The lattice oxygen supplied electrochemically to the catalyst surface actively participated in the oxidation reaction, with CO as the major product, and CO_2, CH_3OH and HCHO as the minor products. The reaction rate was found to be of first order with respect to methane. The rate constant depended strongly on the electrochemically imposed bias. Under DC bias condition, the reaction rate was enhanced by as much as two orders of magnitude over that observed under open-circuit conditions. An Eley–Rideal mechanism for the interaction of CH_4 with surface oxygen is proposed as the rate-determining step.

Keywords: Electrochemical reactor; methane oxidation; zirconia electrolyte; $YBa_2Cu_3O_x$ catalytic electrode; lattice oxygen

1. Introduction

Partial oxidation of methane to valuable chemical feedstock and fuels is of great interest. Although the free energy changes associated with the oxidation of methane (see table 1) indicate the feasibility of producing intermediate oxidation products such as methanol, formaldehyde and carbon monoxide, heterogeneous reaction kinetics with various catalysts have favored carbon dioxide production. Solid state electrochemical studies using ionically conducting solid electrolytes have provided an interesting new approach to modify catalyst reactivity and selectivity. Earlier examples of this approach using noble metal and metal oxide catalytic electrodes on solid oxide electrolytes include the epoxidation of olefins [2,3] and the oxidation of methane [4–6] as recently reviewed by Eng and Stoukides [7].

A number of complex metal oxides with perovskite structure have been found suitable as oxidation catalysts [8] because they exhibit a wide range of oxygen nonstoichiometry without concomitant phase changes, a high density of electronic

Table 1
Gibbs free energy changes for methane oxidation [1]

Reaction	ΔG_{rxn} (kJ/mol)	
	298 K	1000 K
(1) $CH_4 + 2O_2 = CO_2 + 2H_2O$	−802.1	−801.9
(2) $CH_4 + \frac{3}{2}O_2 = CO + 2H_2O$	−544.9	−606.2
(3) $CH_4 + O_2 = CH_2O + H_2O$	−288.4	−300.6
(4) $CH_4 + \frac{1}{2}O_2 = CH_3OH$	−115.6	−73.1

defects, and significant oxygen-ion mobility. Of special interest to this study is the high temperature superconductor $YBa_2Cu_3O_x$, whose oxygen stoichiometry (subscript x) may vary over an unusually wide range between 6.0 and 7.0 [9]. Accordingly, this material has the ability to serve as an oxygen source for the catalytic reaction since the oxygen ions are quite mobile in the defect lattice of this mixed-conductor and contribute to the total charge transport at elevated temperatures. The chemical diffusion coefficient for oxygen in this material has a value of 5×10^{-8} cm^2 s^{-1} at 1073 K [10]. Earlier measurements using the oxygen coulometric titration technique in a solid state electrochemical cell have established the stability and phase equilibria [11,12] in this quaternary system and the strong dependence of its superconducting properties on the oxygen stoichiometry [13].

The exceptionally wide range of oxygen nonstoichiometry and the high transport rate of oxygen make $YBa_2Cu_3O_x$ a potentially attractive oxidation catalyst. In fact, Hansen et al. [14] recently studied the conversion of toluene catalyzed by $YBa_2Cu_3O_x$ and reported that at low oxygen pressures, i.e., large oxygen deficiency, the catalyst was selective for the formation of benzonitrile, whereas oxidation to CO_2 was preferred at high oxygen pressures. The present study concerns the partial oxidation of methane catalyzed by the $YBa_2Cu_3O_x$ electrode in a solid state electrochemical reactor employing yttria-stabilized zirconia (YSZ) as a solid oxide electrolyte.

2. Experimental

The schematic diagram of the electrochemical reactor is depicted in fig. 1. A 12 inch long, 3/8 inch o.d. yttria stabilized zirconia (YSZ) tube having the composition $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$ was used for this purpose. The tube was placed inside a quartz jacket about 1 inch in diameter such that the open end of the tube was exposed to the ambient air. Platinum paste (Hanovia #6929) was coated on the inside surface at the closed end and fired at about 1120 K in air for 1 h to form a porous, contiguous, and adherent Pt electrode layer. This Pt electrode, exposed to the ambient atmosphere, served as the reference electrode with a fixed oxygen activity. The $YBa_2Cu_2O_x$ was deposited on the outer surface of the YSZ tube at the

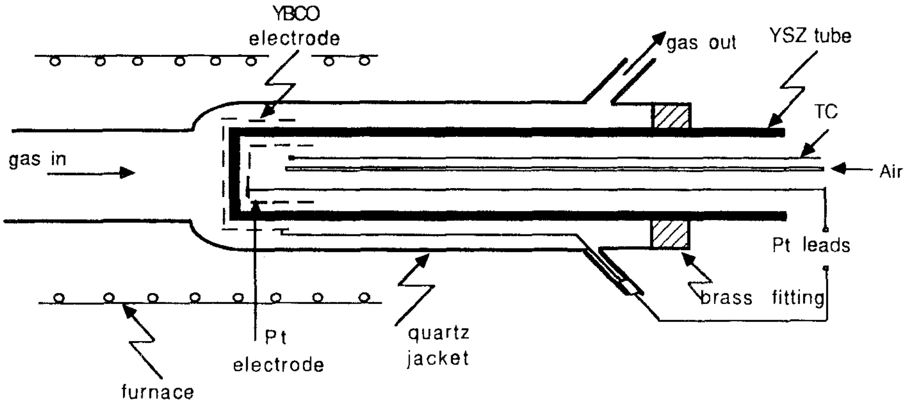

Fig. 1. Schematic design of the solid state electrochemical reactor employing a YSZ solid electrolyte.

closed end by applying the finely divided $YBa_2Cu_3O_x$ powder dispersed in a high molecular weight organic vehicle as a paste and firing it at 1120 K in air for 1 h to form an adherent electrode layer about 50 μm in thickness. It served as the catalytic surface for the partial oxidation of methane. The resulting electrochemical reactor configuration can be represented by

$$(+) \quad CH_4, YBa_2Cu_3O_x/YSZ/Pt, air \quad (-) . \tag{1}$$

The oxygen participating in the oxidation of methane was transported electrochemically through the YSZ solid electrolyte from the negative electrode in contact with air to the positive electrode in contact with methane. This process involves the dissociative adsorption of oxygen on the Pt electrode followed by the interaction of oxygen atoms with oxygen-ion vacancies and electrons at the negative electrode, as represented by

$$O(a) + V_O^{\infty} + 2e' = O_o^x , \tag{2}$$

where O(a) is adsorbed oxygen, V_O^{∞} denotes an oxygen vacancy in the YSZ electrolyte, and O_o^x is an occupied oxygen ion lattice site in YSZ. The oxygen ions are transported under the imposed potential through the YSZ electrolyte toward the positively biased $YBa_2Cu_3O_x$/YSZ interface. This interface is sustained at high oxygen activity by the externally imposed potential. The oxygen consumed in the chemical oxidation process at the $YBa_2Cu_3O_x$ surface arrives by chemical diffusion through the steep chemical potential gradient across the thickness of the $YBa_2Cu_3O_x$ layer. At constant applied voltage the current flowing in the external circuit provides a quantitative measure of the rate of oxygen transport during reaction, since YSZ is predominantly an oxide ion conducting electrolyte.

The electrochemical reactor was an integral part of a gas-management and recirculating system which was described in detail in a previous study [15]. It had a total internal volume of 115 ml, and contained several zero-dead-volume multiport valves for injecting reactant gases, changing reactor operation from flow-through to recirculation mode, and withdrawing samples for chemical analysis by gas chromatography (HayeSep R column material) and mass spectroscopy. In this study the experiments were made in the recirculating mode. Before each run, however, the system was flushed in the flow-through mode overnight with oxygen to ensure that the oxygen stoichiometry of the $YBa_2Cu_3O_x$ electrode was at its equilibrium value at the temperature of the experiment. Subsequently, the O_2 flow was replaced by He (99.99 vol%) in order to rapidly flush the oxygen out of the system. After switching to the recirculating mode, known quantities (typically 10 ml at NTP) of CH_4 (99.99%) were injected into the reactor. A suitable DC bias (typically 1 or 2 V) was imposed across the electrolyte and maintained throughout the duration of the experiment. In some of the experiments, small quantities of O_2 (typically 2 ml at NTP) were added to the reaction mixture through a multiport valve in order to study the effect of gas phase O_2 on the oxidation kinetics.

In order to monitor the chemical stability of the $YBa_2Cu_3O_x$ electrode during the course of the experiments, open-circuit voltages were measured intermittantly by interrupting the imposed DC bias. They were found to be positive with respect to air, indicating that the effective oxygen activity at this interface was higher than 0.21 atm where $YBa_2Cu_3O_x$ is known to be stable at these temperatures [11,12].

3. Results and discussion

During a typical experiment, the reactant gas mixture (CH_4 + He) was recirculated through the electrochemical reactor under open circuit or DC biased conditions and the conversion of CH_4 was monitored intermittently. Gas chromatographic evidence showed that carbon monoxide is the major carbon-containing product. In addition to CO, the other partial oxidation products identified by mass spectrometric analysis were formaldehyde (29 amu) and methanol (31 amu) as shown in fig. 2. Their concentrations were small relative to CO and favored at the lower temperatures of the study. Although oxygen was continuously pumped to the $YBa_2Cu_3O_x$ electrode surface, no accumulation of gas phase O_2 in the reactor was observed. It was consumed entirely in the oxidation of CH_4. The presence of a 47 amu peak was detected in those experiments in which gaseous O_2 was added deliberately to the reactor. This peak suggests the presence of CH_3OOH. Another signal at 50 amu has not yet been identified.

The disappearance of the CH_4 peak followed an exponential decay indicative of first-order kinetics (fig. 3). The rate constants for the oxidation of methane derived from these measurements over a range of temperatures and applied DC potentials are summarized in table 2. Based on this data, an activation energy for methane oxidation is found to be 90 kJ/mol. Its value is not affected by the magnitude of the DC bias applied to the electrochemical cell over the range studied. How-

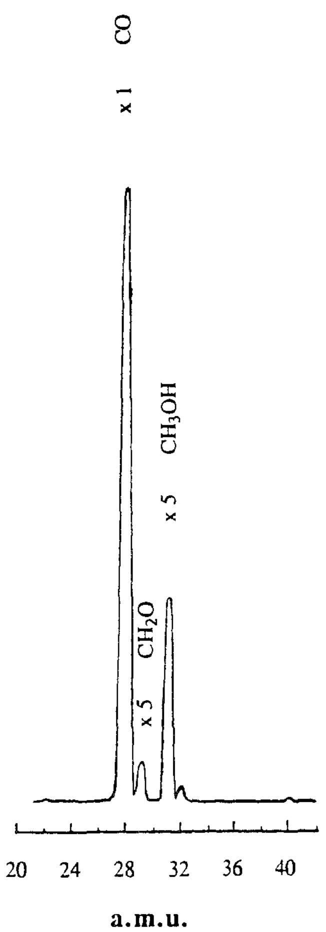

Fig. 2. Mass spectra showing methanol and formaldehyde formation after 17 min during an experiment at 1010 K and 2 V bias using a CH_4 + He reaction mixture.

ever, the rate constants are strongly dependent upon the bias condition and increase significantly with applied voltage. At 2 V and 1000 K, it exceeds by more than two orders of magnitude the value measured under open-circuit condition.

An important finding of the present study is the participation of the electrochemically supplied oxygen in the oxidation reaction on the $YBa_2Cu_3O_x$ catalyst electrode. The introduction of gas phase O_2 into the CH_4 + He reaction gas mixture resulted primarily in the formation of carbon dioxide, in contrast to carbon monoxide and intermediate products that formed when the CH_4 + He reaction mixture was oxidized by the electrochemically supplied oxygen. The first-order kinetics of the reaction can be interpreted in terms of an Eley–Rideal mechanism involving the interaction of a methane molecule with surface oxygen as the rate-determining step.

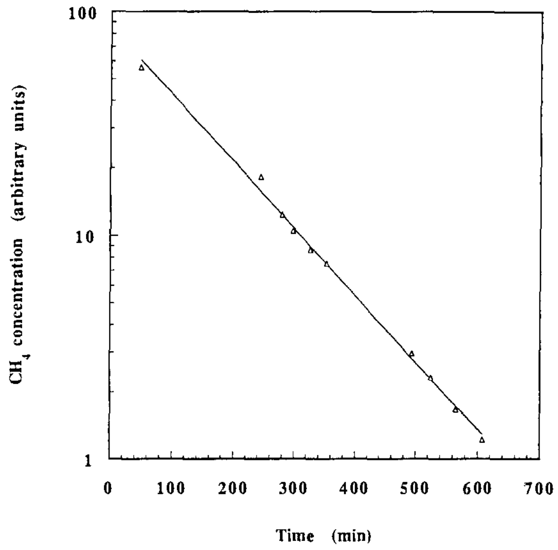

Fig. 3. Time dependent change in the concentration of CH_4 indicating first order kinetics at 840 K and 1.5 V DC bias using a CH_4 + He reaction mixture.

4. Summary

Methane was partially oxidized on a $YBa_2Cu_3O_x$ catalyst electrode in a solid state electrochemical reactor. The predominant carbon-containing product was carbon monoxide with lesser amounts of carbon dioxide, methanol, and formalde-

Table 2
Reaction rate constants, k_{CH_4} (s^{-1}), for methane oxidation under open circuit (OCV) and DC bias conditions

T(K)	OCV	$E = 1$ V	$E = 1.5$ V	$E = 2$ V
CH_4 + He feed				
840			1.2×10^{-4}	
860			4.0×10^{-5}	
910		1.4×10^{-4}		1.9×10^{-4}
				2.2×10^{-4}
1010		9.3×10^{-4}		2.7×10^{-3}
1050	7.2×10^{-5}			
1070	7.7×10^{-5}			
1110		8.7×10^{-4}		1.1×10^{-3}
CH_4 + O_2 + He feed				
920		2.2×10^{-4}		
		2.6×10^{-4}		
1010		1.2×10^{-3}		
		1.1×10^{-3}		

hyde. The reaction rates were found to be dependent on the electrochemically imposed bias conditions and enhanced by as much as two orders of magnitude over the rates under open circuit conditions. The lattice oxygen supplied electrochemically through the $YBa_2Cu_3O_x$ electrode was crucial for the observed selective partial oxidation.

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