

NOTES

Methane Oxidation by Oxygen Transported through Solid Electrolyte

Solid oxide electrolytes such as yttria-stabilized zirconia, doped ceria, and β -phase bismuth oxide are well known as good oxygen ion conductors. Applications of this high ionic conductivity have been made to fuel cells, oxygen pumps (1), oxygen sensors (2), and reactors for various kinds of catalytic reactions (3-8). Recently, an attempt has been made to utilize oxygen ions transported through a solid electrolyte to a catalyst electrode for the oxidative coupling of methane (9). It has been reported that oxygen transported to Bi_2O_3 -Ag catalyst at low transport rates showed higher activity and selectivity for production of C_2 compounds (ethane and ethylene) than oxygen supplied from the gas phase. However, over an Ag electrode such high selectivity was not obtained.

In the present work, the oxidation of methane was carried out over a single electrode in order to escape from the complexity which arises from the coexistence of electrode and catalyst. Silver pastes and lanthanum cobaltate powders were employed as electrode materials, because these materials are known to catalyze partial and deep oxidation, respectively.

The solid electrolyte tubes, made of zirconia doped with 8 mol% yttria (yttria-stabilized zirconia (YSZ)), were purchased from the Nippon Kagaku Togyo Co. Their dimensions were 5 mm ID, 8 mm OD, and 30 cm length. Silver electrodes were made from silver paste (Engelhard, #16) and averaged about 5 μm in diameter. LaCoO_3 electrodes were made from their fine powder prepared from an aqueous solution of the metal nitrates by the coprecipitation method (10). The closed-end electrolyte tube was in-

serted into an outer tube made of mullite. The catalyst electrode was situated at the center of the outer tube. The area of the catalyst electrode was 15.1 cm^2 . Oxygen at 0.1 MPa was supplied into the electrolyte tube.

A flow of methane diluted to 20% with helium was supplied outside the electrolyte tube. The flow rate on the catalyst electrode side was maintained at 50 ml min^{-1} . Reactants and products such as CO, H_2 , CO_2 , C_2H_6 , C_2H_4 , and C_3H_8 were analyzed by a gas chromatograph (GC-8A, Shimadzu, 90°C) with Unibeads 1S and Molecular Sieve 13X columns. A material balance within $\pm 5\%$ was achieved for carbon.

To compare the reactivity of the transported oxygen with that of oxygen in the gas phase, the following three reaction systems were employed: (1) Transport system, where the reaction is caused by oxygen transported electrochemically. (2) Mixture system, where the reaction is caused by oxygen premixed in the gas phase. (3) Joint system, where both transported and premixed oxygen taken part in the reaction.

RESULTS AND DISCUSSION

The open circuit voltage at the methane pressure of 0.1 MPa was 0.83 V at 1008 K, which was little lower than the value calculated from thermodynamic data. This suggested small leakage of oxygen into the reactor. The reaction with the transported oxygen was performed by potentiostatically applying an external voltage between the two electrodes. Figure 1 shows the conversion of oxygen over the Ag electrode at 1008 K as a function of the oxygen feed rate. The conversion of the transported oxygen was

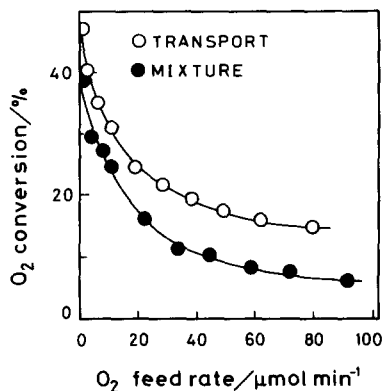


FIG. 1. Oxygen conversion over Ag electrode at 1008 K as a function of oxygen feed rate.

greater than that of premixed oxygen. It was shown that the smaller conversion of the premixed oxygen was not due to the mass transfer limitation of oxygen in the gas phase, since the oxygen conversion over LaCoO₃ was close to unity.

The main products were CO₂, C₂H₆, and C₂H₄. Formation of CO was negligibly small. Figure 2 shows the formation rate of C₂ compounds over the Ag electrode at 1008 K. The C₂ formation rate clearly increased with the oxygen feed rate or the applied

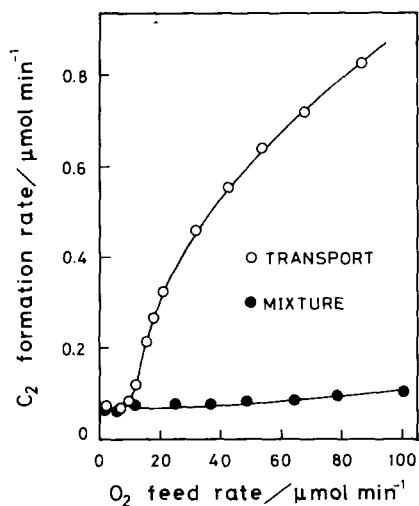


FIG. 2. C₂ formation rates over Ag electrode at 1008 K as a function of oxygen feed rate.

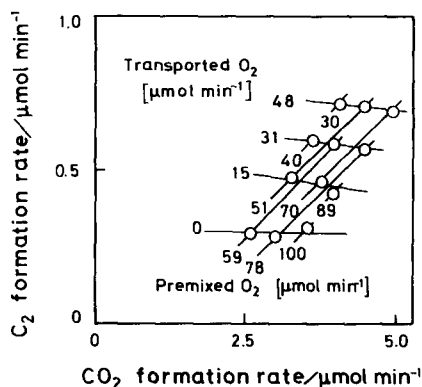


FIG. 3. Formation rates of CO₂ and C₂ compounds over Ag electrode at 1023 K for the joint system.

voltage for the transport system. In contrast, Otsuka *et al.* observed that the C₂ formation rate decreased at the oxygen feed rates over 30 μmol min⁻¹ in a similar reaction system (9). The C₂ formation at oxygen feed rates over 70 μmol min⁻¹ was over eight times greater for the reaction with transported oxygen than that with premixed oxygen. The almost constant C₂ formation rate for an oxygen feed rate of less than 7 μmol min⁻¹ might be due to the thermal reaction of methane. On the other hand, over LaCoO₃ electrodes the deep oxidation of methane predominantly took place to give C₂ selectivity less than 2%.

Figure 3 shows the variation in formation rates of C₂ compounds and CO₂ caused by changing the feed rates of gaseous oxygen and ionic oxygen. Increasing the gaseous oxygen feed rate did not enhance the formation of C₂ compounds. In fact, a decreasing trend in C₂ formation was observed. On the other hand, CO₂ formation was steadily increased. In addition, without feeding gaseous oxygen, it was verified that decreasing the partial pressure of oxygen by increasing the total flow rate had an effect on the decrease of CO₂ formation.

When the active species of oxygen is not in equilibrium with the gaseous oxygen, two cases can be considered to explain that result. One is that the adsorption-desorption

process is not in equilibrium. The other is that the active species is not the same as adsorbed oxygen in equilibrium with the gaseous oxygen. Based on the fact that the YSZ cell employed worked well as an electrochemical oxygen sensor for the mixture system, the former case does not apply. Hence the latter case probably does apply.

The activation energies for C_2 and CO_2 formation were measured at temperatures ranging from 953 to 1043 K under the differential reactor condition, where the total flow rate on the catalyst electrode side was increased to 105 ml min^{-1} . The values of the activation energies for the transport system were 130 kJ mol^{-1} for C_2 formation and 125 kJ mol^{-1} for CO_2 formation. Those for the mixture system were 280 kJ mol^{-1} and 196 kJ mol^{-1} , respectively. The difference in the activation energy with respect to the reaction system also suggested that the latter case mentioned above is true.

Vayenas *et al.* reported that under fuel-lean conditions the deep oxidation of ethylene was considerably enhanced by electrochemically pumping oxygen (7). They explained that this phenomenon was caused by the changes in the catalyst work function resulting from the interaction of oxygen anions with the catalyst surface. In the oxidation of methane in the joint system, on the other hand, applying potentials did not enhance either C_2 formation or CO_2 formation so much as they reported. Therefore, the phenomenon observed is considered to be different from those they reported. Further investigation is needed to elucidate the

mechanism of oxidation of methane by transported oxygen.

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