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CATALYTIC ACTIVITY- AND SELECTIVITY-CONTROL FOR OXIDATIVE COUPLING OF METHANE BY OXYGEN-PUMPING THROUGH YTTRIA-STABILIZED ZIRCONIA

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Oxidative coupling of methane over Ag and Bi_2O_3-Ag were carried out by the electrochemically pumped oxygen through yttria-stabilized zirconia at 973 K. The oxygen pumped to the Bi_2O_3-Ag catalyst showed higher catalytic activity and selectivity for the production of C_2-compounds (C_2H_4+C_2H_6) compared to the surface oxygen from gas phase.

The yttria stabilized zirconia is a well known solid-electrolyte in which conduction is due almost entirely to oxygen ion transport in a lattice with anion vacancies. It has been found suitable for a wide range of applications such as high-temperature fuel cells, oxygen sensors, oxygen pumps, and for various thermodynamic and kinetic measurements.$^{1)}$ The current through a cell using yttria-stabilized zirconia (YSZ) as solid electrolyte such as

$$P_{O_2}', \ M / YSZ / M, \ P_{O_2}'' \qquad (\ M;\ \text{electrodes}\ )$$

is a measure of the rate at which oxygen is passed from one side of the cell to the other. Since only oxygen ions can pass through the electrolyte when the electrical circuit through the electron-conducting leads is closed, it also follows that the oxygen pumping across the YSZ can be controlled by the electric potential externally applied between the both electrodes. The relation between the oxygen transfer flux (J) from one electrode to the other and current density (I) can be written as follows,

$$I = 2FJ \qquad (1)$$

where F is the Faraday constant. The applications of zirconia cells for the catalytic reactions such as NO decomposition,$^{2)}$ CO hydrogenation,$^{3)}$ and ethylene oxidation$^{4)}$ on metal catalysts have been demonstrated. Michaels and Vayenas$^{5)}$ claimed the advantages of electrochemical process over the conventional catalytic methods for oxidative dehydrogenation of ethylbenzen on silver.

The primary interest in this work is to carry out catalytic oxidative coupling of methane ($CH_4 + O_2 \rightarrow C_2H_6, C_2H_4 + H_2O$) by the oxygen transferred through YSZ. Methane, one possible raw material, is the most abundant component of natural gas. Therefore, it represents a considerably more abundant precursor for ethylene than ethane and propane which are the two most widely used gaseous precursors. Shortage of these precursors for ethylene manufacture have promoted us to use methane as the precursor of ethylene. The second purpose in this work is to investigate whether the surface oxygen generated electrochemically through YSZ would have higher catalytic activity and selectivity for oxidative coupling of methane compared to those of the surface oxygen which is supplied directly from gas phase under open circuit conditions.

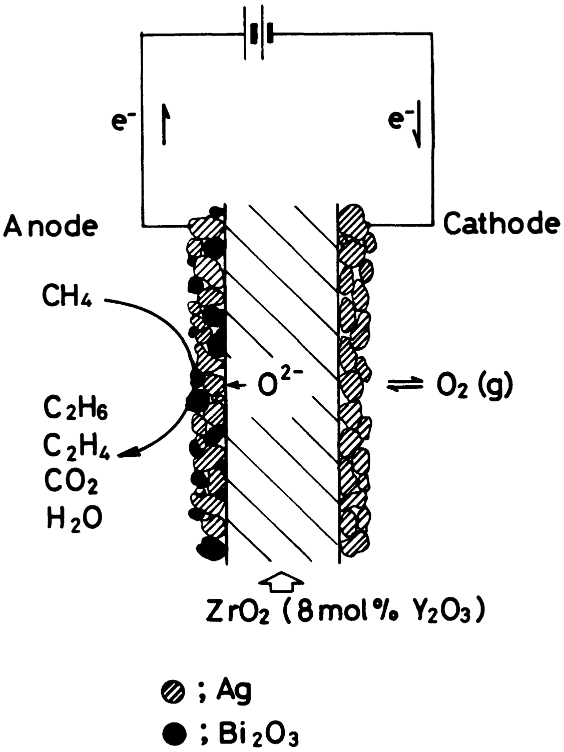

Fig. 1. Schematic diagram of the reaction system.

The experimental apparatus has been described in detail elsewhere.⁶⁾ The schematic diagram of the reaction system is shown in Fig. 1. The catalysts tested were Ag and Bi_2O_3-Ag where Ag worked also as electrodes. Preliminary experiments revealed that the Bi_2O_3-Ag was one of the most favorable catalysts for oxidative coupling of methane. The method of adhesion of the silver-electrodes on YSZ was described elsewhere.⁶⁾ The Bi_2O_3-Ag catalyst was prepared by coating the silver electrode with the Bi_2O_3 powder suspended in acetone. Before the experiments the catalysts were treated in a flow of oxygen at 873 K. The geometrical areas of the catalysts were 6.6 cm^2 on YSZ. The reaction was carried out using a conventional gas-flow system under atmospheric pressure. Methane was diluted with helium (CH_4/CH_4+He = 0.20). The feed rate of methane at the anode side was 4.2 ml min^{-1}. The oxygen of 101.3 kPa was always maintained on the cathode of the cell.

Oxidative coupling of methane over Ag electrode (catalyst) was first examined at 973 K. The open-circuit voltage for the cell was 0.563 V. The reaction took place when the circuit was closed by connection of silver lead-wires from both electrodes; the free-energy change accompanied by the reaction is the driving force for the transfer of oxygen across the YSZ. Figure 2 shows the rates of formation of products as functions of the flux of oxygen which was controlled by the electric potential applied between the electrodes. There were no detectable alcohols and aldehydes produced. The carbon- and oxygen-balances for the reaction were good within the experimental error of ±6%. The symbol (◑) in Fig. 2 indicates the rate of evolved oxygen to gas phase without reaction with methane. The selectivity of C_2-compounds (C_2H_4 + C_2H_6) at zero externally applied potential under closed circuit was 52% on the basis of carbon of methane converted. The selectivity(dotted curve) decreased sharply with increasing the oxygen flux. The decrease in the selectivity of C_2-compounds under high oxygen pressure can be ascribed to the burning of the C_2H_6 and C_2H_4 produced. Therefore, the reaction should be operated under low pumping speed of oxygen as far as the selectivity of C_2-compounds is concerned.

The results for the Bi_2O_3-Ag catalyst at 973 K are shown in Fig. 3. The reaction did not proceed when the circuit was not closed. The rates of formation of

C_2-compounds were considerably greater for this catalyst compared to the rates observed for Ag catalyst (Fig. 2) under same flux of oxygen pumped. The selectivity of C_2-compounds is also greater for the Bi_2O_3-Ag than for the Ag catalyst (see Figs. 2 and 3). The selectivity at zero applied potential is 67% which is a quite high value ever reported.[7,8] The results in Fig. 3 show that the oxidative coupling of methane should be conducted under the oxygen flux of ca. 12 µmol min^{-1} (the corresponding applied potential is 1.3 V) which gives the maximum rate of formation of C_2-compounds and high selectivity of the C_2-products (47%).

The reaction for the mixture of methane and oxygen was carried out on the same Bi_2O_3-Ag used in the experiments of Fig. 3, under open circuit conditions where no oxygen was pumped through the YSZ. The rate of conversion of methane (◇) and that of the formation of C_2-compounds (△) are plotted in Fig. 4 as functions of the feed rate of oxygen. The value of the closed symbols in Fig. 4 are evaluated from Fig. 3 for the reaction with the electrochemically pumped oxygen, where the feed rate of oxygen is the flux of oxygen supplied through YSZ. The results in Fig. 4 show that the surface oxygen which is supplied electrochemically produces C_2-compounds more selectively than does the surface oxygen from gas phase under the feed rate of oxygen lower than 25 µmol min^{-1}. Higher rates of conversion of methane are also observed for the former under lower feed-rate of oxygen than 20 µmol min^{-1}. The electric potential applied across the YSZ may enhance the activity of surface oxygen as well as influence the nature of the active sites on the catalyst, which may explain the favorable action of the electrochemically pumped oxygen described above. However, the catalytic activities as well as the selectivities of C_2-compounds observed in the two methods become closer together as the feed-rate of oxygen increases (>20-25 µmol min^{-1}). The characteristic feature of the reaction due to the electrochemically pumped oxygen may be extinguished by the oxygen accumulated in gas phase when the flux of electrochemically pumped oxygen through YSZ increases. In the case of Ag described earlier, there were no difference in the catalytic activities or selectivities of C_2-compounds observed in the two methods at any feed rate of oxygen. The details of the reaction mechanism, the nature of active sites,

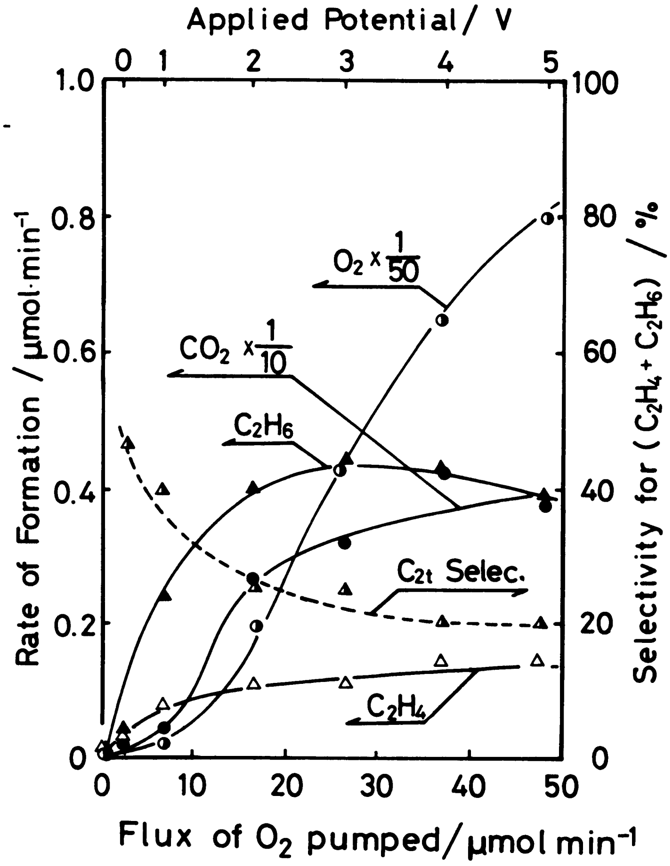

Fig. 2. The rates of formation of products on Ag and the selectivity of C_2-compounds as functions of oxygen flux through YSZ: The rate of formation of CO_2 and that of O_2 evolved are reduced by a factor of 10 and 50, respectively.

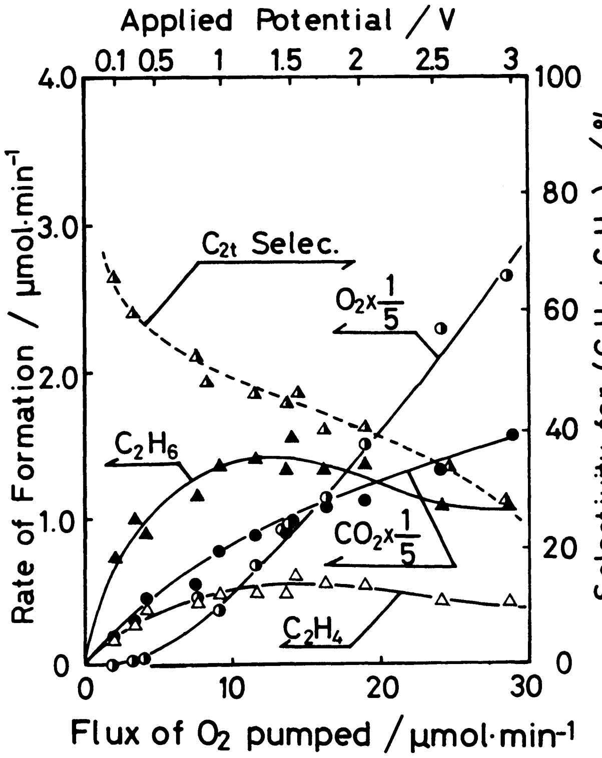

Fig. 3. The rates of formation of products on Bi_2O_3-Ag and the selectivity of C_2-compounds as functions of the flux of oxygen through YSZ: The scales for the rate of formation of CO_2 and that of O_2 evolved are reduced by a factor of 5.

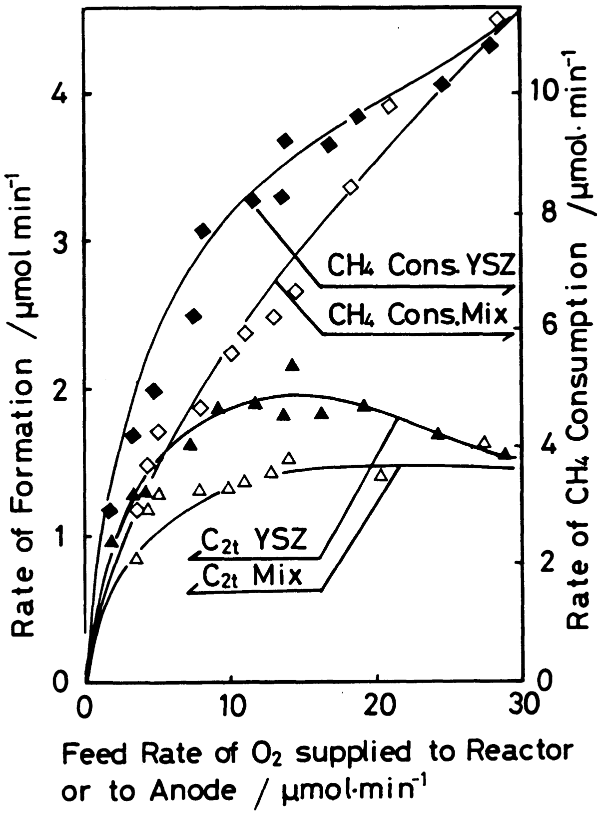

Fig. 4. Comparison of the results obtained in the usual catalytic reaction (Mix-method) and in the electrochemically controlled reaction (YSZ-method) for the Bi_2O_3: Mix-method: △, C_2-compounds; ◇, CH_4. YSZ-method: ▲, C_2-compounds; ◆, CH_4.

and the effect of electric potential on the reaction, are not known at the moment. Further studies are needed to clarify these points.

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