Catalysis Letters 1 (1988) 423–428

ELECTROCHEMICAL ENHANCEMENT OF OXIDATIVE COUPLING OF METHANE OVER LiCl-DOPED NiO USING STABILIZED ZIRCONIA ELECTROLYTE

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Received 22 August 1988; accepted 25 October 1988

Oxidative coupling of methane into ethylene and ethane over LiCl-doped NiO was enhanced when oxygen was pumped electrochemically to the catalyst through a stabilized zirconia oxygen-anion conductor. This favourable effect can be ascribed to the generation of reactive oxygen species on the catalyst for selective synthesis of C_2 compounds.

1. Introduction

Partial oxidation of methane into higher hydrocarbons is one of the most attractive ways of utilizing natural gas as a chemical resource. Oxidative coupling of methane to C_2H_6 and C_2H_4 is currently the subject of considerable research interest [1]. We have found that the LiCl-doped NiO (denoted as LiCl/NiO hereafter) is a selective catalyst for this reaction [2,3]. NiO without LiCl catalyzes only the deep oxidation of methane to CO and CO_2. Addition of LiCl, however, inhibits the catalytic activity of the host NiO in the conversion of methane, particularly the deep oxidations of CH_4, and C_2 compounds are produced. Although the added LiCl improves the C_2 selectivity, the catalytic activity for C_2 formation is not satisfactory.

The application of an electrochemical technique utilizing a stabilized zirconia solid electrolyte to the partial oxidation of hydrocarbons was first demonstrated by Stoukides and Vayenas [4]. Otsuka et al. [5] have applied this technique to the partial oxidation of methane over the Ag- or Bi_2O_3/Ag-deposited zirconia electrolyte. The reaction rate and the selectivity to C_2-compounds ($C_2H_6 + C_2H_4$) could be controlled by the flux of oxygen electrochemically pumped through the zirconia electrolyte. In this letter, we describe the application of this technique to the oxidative coupling of methane over LiCl/NiO in order to improve the selectivity and the catalytic activity of the catalyst for the synthesis of C_2-compounds.

2. Experimental

Yttria-stabilized zirconia plates ($20 \times 14 \times 0.4$ mm^3) obtained from Nippon Kagaku Togyo were used in the experiments. Fine NiO powder obtained from Wako Pure Chemical company was immersed into the aqueous solution of LiCl. The solution with NiO was dried at 373 K and 673 K for 2 h. The mol ratio of LiCl and NiO was adjusted to 1 : 5. The LiCl-doped NiO was finally calcined in air at 973 K for 2 h, and the LiCl/NiO powder thus prepared was suspended in acetone. This catalyst suspension was spread onto one of the Au-electrodes which had been deposited on both sides of the zirconia plate by a vapour deposition technique. The catalyst with acetone on the Au-electrodes was dried at 433 K and calcined in the flow of mixture of He and O_2 (4 : 1) at 973 K for 2 h.

The catalytic tests of the LiCl/NiO for partial oxidation of CH_4 were carried out using a conventional gas-flow system under atmospheric pressure using helium as a carrier gas. Flow rate of the gas mixture were in the range of 20 to 50 mlSTP min^{-1}.

The catalyst-deposited zirconia plate was suspended in a flow of the gas mixture of methane and oxygen as demonstrated in fig. 1. Under open circuit conditions LiCl/NiO acted as a regular catalyst for oxidative coupling of methane. Under externally applied voltage between the two electrodes, O^{2-} is pumped through the zirconia electrolyte to or from the catalyst depending on the polarity of the applied potential.

The conversion of CH_4 and the selectivities of products were calculated on the basis of carbon number of the methane reacted.

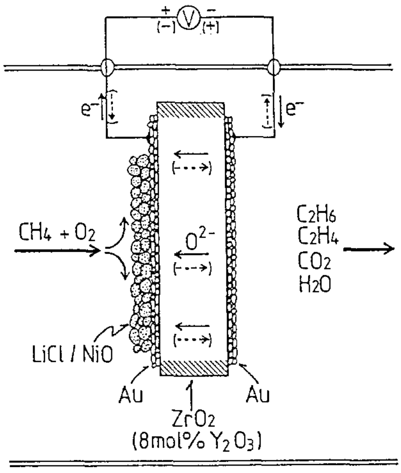

Fig. 1. Schematic diagram of the electrochemical control of the partial oxidation of CH_4 using the LiCl/NiO catalyst on he Au-deposited stabilized zirconia.

3. Results

(a) EFFECT OF O^{2-} PUMPING

Figure 2 shows the formation rates of products, O_2 conversion and C_2 selectivity ($C_2H_6 + C_2H_4$) as functions of the current, the corresponding externally applied voltages are also shown. Deactivation of the catalyst probably due to the loss of LiCl [3], was serious at the early stage of the reaction at higher temperatures than 973 K, but constant activity was observed after 3 h. Steady state results were obtained within 20 min after changing the current (or applied voltage) from one steady value to the other. Positive current in fig. 2 means that O^{2-} is pumped from the right side of zirconia to the catalyst in fig. 1, and negative current involves the pumping from the catalyst to the right. The results in fig. 2 show that the oxygen pumping to the catalyst increases the formation rates of C_2H_6 and C_2H_4 and favorably decreases the rate of CO_2 formation, thus improving the C_2 selectivity up to 92% at the current of +80 mA. On the other hand, the oxygen pumping from the catalyst to the other side of the zirconia plate did not change appreciably the formation rates of the products from those observed under open circuit conditions. When the current was lowered below −30 mA (applied voltage < -0.7 V), the catalyst became unstable and the catalytic results were irreproducible.

The conversion of both oxygen and methane is increased with a rise in the flux of oxygen pumped to the catalyst. The increase in the amount of oxygen consumed under closed circuit conditions can be estimated from the difference in

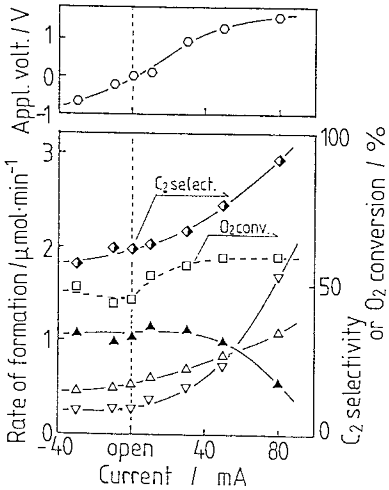

Fig. 2. Effects of oxygen pumping on the rates of products, C_2 selectivity and O_2 conversion. ○, applied voltage; △, rate of C_2H_6 formation; ▽, rate of C_2H_4 formation; ▲, rate of CO_2 formation; □, O_2 conversion; ◆, C_2 selectivity. Reaction conditions: $T = 973$ K, $P(CH_4) = 15$ kPa, $P(O_2) = 0.52$ kPa, total flow rate = 20 mlSTP min^{-1}, weight of LiCl/NiO = 0.10 g.

the oxygen conversions under closed and open circuit conditions (fig. 2). If the increase in the consumption of oxygen is due wholly to the reaction of the pumped oxygen to the catalyst with methane, it follows that 22% and 5% of the oxygen pumped were used in the reaction at the constant current of +10 and +80 mA, respectively, in fig. 2. The current efficiency of the pumped oxygen used in the reaction was not high.

The Au-electrodes on the zirconia without the LiCl/NiO catalyzed only a slow deep oxidation of CH_4 irrespective of the open or the closed circuit conditions. The absolute rate of this reaction was less than 5% of that observed in the presence of the LiCl/NiO at any temperatures.

(b) EFFECT OF REACTANT PRESSURE

The rates of CO_2 and C_2 formations and the C_2 selectivity observed at 913 K under open and closed circuit (O^{2-} pumping of +20 mA) conditions are plotted against CH_4 pressure in fig. 3. The C_2 selectivity increased with a rise in the CH_4 pressure irrespective of open and closed circuit conditions. However, this increase was relatively larger under closed circuit conditions compared to that observed under open circuit.

Figure 4 shows the effects of oxygen pressure on the selectivities and the formation rates of products observed under open and closed circuit conditions. The results in the figure show that the favorable effect of oxygen pumping to the catalyst with +20 mA constant current is enhanced with a decrease in the pressure of oxygen, i.e., the increase and the decrease in the formation rates of C_2

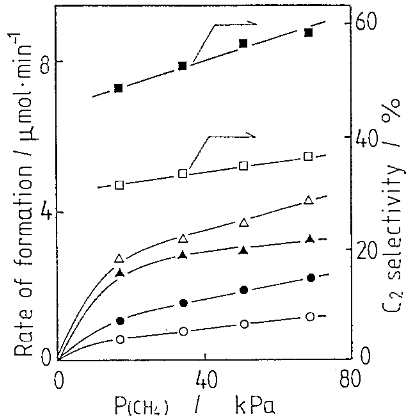

Fig. 3. Effects of CH_4 pressure on the rates of C_2 formation and C_2 selectivity under open and closed circuit conditions. Open circuit: ○, rate of C_2 formation; △, rate of CO_2 formation; □, C_2 selectivity. Closed circuit with +20 mA current: ●, rate of C_2 formation; ▲, rate of CO_2 formation; ■, C_2 selectivity. Reaction conditions: $T = 913$ K, $P(O_2) = 10.1$ kPa, total flow rate = 30 mlSTP min^{-1}, LiCl/NiO = 0.12 g.

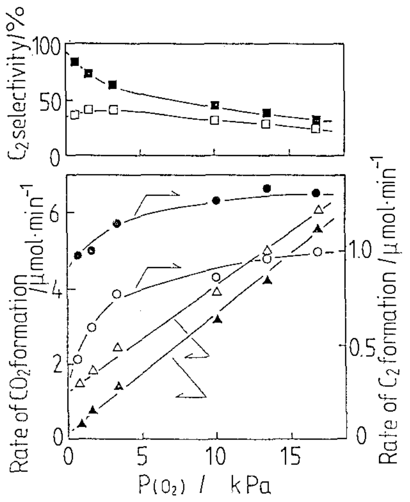

Fig. 4. Effects of O_2 pressure on the rates of C_2 and CO_2 formations and on the C_2 selectivity under open and closed circuit conditions. The meanings of the symbols are the same as those in fig. 3. Reaction conditions: $T = 913$ K, $P(CH_4) = 33.7$ kPa, total flow rate = 30 mlSTP min^{-1}, LiCl/NiO = 0.19 g.

and CO_2, respectively, were promoted at the low pressure range of oxygen, improving the C_2 selectivity.

(c) TEMPERATURE EFFECT ON THE FORMATION RATES OF PRODUCTS

Figure 5 shows the plot of logarithm of formation rates (R) of C_2 and CO_2 against inverse of temperature. The apparent activation energies calculated from the slopes of the lines in fig. 5 are as follows: for CO_2 formation, 114 (open) and

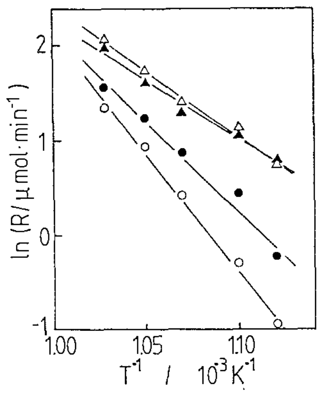

Fig. 5. Temperature effects on the formation rates of products measured under open and closed circuit conditions. Open circuit: ○, C_2 formation; △, CO_2 formation. Closed circuit with +20 mA current; ●, C_2 formation; ▲, CO_2 formation. Reaction conditions: $P(CH_4) = 33.7$ kPa, $P(O_2) = 10.1$ kPa, total flow rate = 30 mlSTP min^{-1}, LiCl/NiO = 0.10 g.

101 kJ mol^{-1} (O^{2-} pumping at +20 mA current); for C_2 formation, 208 (open) and 154 kJ mol^{-1} (+20 mA current). These observations show that the oxygen pumping decreases the apparent activation energy in the formation of C_2 compounds appreciably compared to the effect of the pumping on the activation energy of CO_2 formation.

4. Discussion

The results in figs. 2 to 4 showed that the O^{2-} pumping to the LiCl/NiO enhances the formation rate of C_2 compounds and reduces CO_2 formation. The O^{2-} pumping decreases the apparent activation energy for the C_2 formation considerably (fig. 5). These observations may be explained by the assumption that the O^{2-} pumped through the zirconia generates reactive oxygen species (O^*) for selective synthesis of C_2 compounds on the LiCl/NiO surface. This active oxygen may adsorb competitively with the oxygen responsible for deep oxidation of CH_4 on the same sites, which explains the observation that the O^{2-} pumping reduces the CO_2 formation. The activation energy for the abstraction of H from CH_4 by the electrochemically generated oxygen (O^*) must be smaller than that by the oxygen responsible for the activation of CH_4 under open circuit conditions. However, it is premature to speculate upon the nature of the O^* species from the present work alone.

We cannot exclude the alternative explanation that the favorable effect of the oxygen pumping is ascribable to the change in the oxidation state of the catalyst under externally applied potential. The number of active sites (probably Ni^{3+} [3]) could be increased under applied potential. Further studies are needed to clarify these points.

The method demonstrated in this work is simple and generally applicable for enhancing the catalytic, partial oxidation of methane using a conventional gas flow system.

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