Catalytic Oxidative Coupling of Methane with a Dark Current in an Electric Field at Low External Temperature

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Abstract—Oxidative coupling of methane (OCM) assisted by a dark current in an electric field was investigated at low external temperature (423 K). The Sr-La$_2$O$_3$ catalyst showed higher yield of C$_2$ (C$_2$H$_4$, C$_2$H$_6$) in the electric field than in the conventional catalytic reaction. Catalytic properties in the electric field and electrical properties of the catalyst were investigated. Results show that the electrical conductivity of dark current of the catalyst is an important factor for applying the electric field. A higher CH$_4$/O$_2$ ratio enabled high selectivity to C$_2$ hydrocarbons. The maximum selectivity to C$_2$ hydrocarbons was 59%.

Keywords—Dark current, electric field, catalytic reaction, natural gas conversion

I. INTRODUCTION

Catalytic oxidative coupling of methane (OCM) is a highly difficult selective oxidation reaction. It has received considerable attention for three decades because highly valuable C$_2$ hydrocarbons, especially ethylene, are generated in this single reaction (Eq. (1)).

\[
\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \frac{1}{2}\text{C}_2\text{H}_4 + \text{H}_2\text{O} \quad \Delta H^\circ = -140 \text{ kJ mol}^{-1}
\]

(1)

Oxide catalysts such as Li/MgO, Mn/Na$_2$WO$_4$/SiO$_2$, and La$_2$O$_3$ have been investigated for reactions [1–10]. CH$_4$ activation on these oxide catalysts requires higher temperature of 973 K because CH$_4$ has tetrahedral stable structure and high CH$_3$-H bond dissociation energy (435 kJ mol$^{-1}$). The rate-determining step of OCM reaction is the activation of CH$_4$. The C$_2$ production reaction includes H-abstraction from CH$_4$ by surface oxygen species, and CH$_3$ coupling in gas phase. Although CH$_3$ formation reaction has high activation energy, CH$_3$ coupling proceeds with almost zero activation energy because of radical reactions [5]. C$_2$H$_4$ is produced by dehydrogenation of C$_2$H$_6$. Aside from C$_2$ production, CO and CO$_2$ are generated by both gas-phase and catalytic oxidation from CH$_4$ and C$_2$ products.

Considering this reaction mechanism, a reaction temperature higher than 973 K is necessary for increasing CH$_4$ conversion. Gas phase oxidation with O$_2$ to form CO and CO$_2$ is not avoidable at high temperatures (over 973 K). To overcome this difficulty, several non-conventional OCM reactions have been performed [11–15]. One example is the OCM reaction using low-energy pulse (LEP) discharge [11–13]. In this process, CH$_4$ is activated by non-equilibrium plasma generated between two electrodes. In the plasma, CH$_4$ is decomposed to C or CH, which is a precursor of C$_2$H$_2$ or the carbon deposition, so C$_2$ production from CH$_4$ included formation of much amount of C$_2$H$_2$, which is not attractive as a chemical feedstock. Additionally, carbon deposition between electrodes caused a short circuit.

Catalytic reactions assisted using a dark current in a DC electric field at low external temperature [16–20] have been studied, with results revealing that the system worked with less energy than either a plasma system or a conventional catalytic system. The catalytic activity was stable for a long time course without carbon deposition in the DC electric field. We applied this system to the OCM reaction. The reaction was able to proceed at low external temperature in the electric field. In this study, the electric field effects were evaluated by examination of the OCM reaction in various experimental conditions. Furthermore, we measured the electrical conductivity to elucidate the electrical property of the catalyst for application of the electric field.

II. METHODOLOGY

Catalytic activity tests with a dark current in the electric field were performed in a fixed bed reactor made of a quartz tube (6, 8 and 10 mm o.d.). Catalysts were charged in it as portrayed in Figure 1. SUS electrodes (2 mm o.d.) were attached on each end of catalyst bed in the quartz tube reactor. Reactant feed gases were CH$_4$, O$_2$, and Ar (CH$_4$/O$_2$/Ar = 25/5/100 mL min$^{-1}$). Water in the effluent stream was removed through a cold trap connected at the reactor outlet. The effluent gas was analyzed using a GC-FID with Porapak N packed column after methanation by Ru/Al$_2$O$_3$ catalyst (for analyses of CH$_4$, CO, CO$_2$, C$_2$H$_2$, C$_2$H$_4$, and C$_2$H$_6$) and a GC-TCD with molecular sieve 5A packed column (for analyses of H$_2$, O$_2$, and N$_2$). Water in the effluent stream was removed through a cold trap connected at the reactor outlet. The effluent gas was analyzed using a GC-FID with Porapak N packed column after methanation by Ru/Al$_2$O$_3$ catalyst (for analyses of CH$_4$, CO, CO$_2$, C$_2$H$_2$, C$_2$H$_4$, and C$_2$H$_6$) and a GC-TCD with molecular sieve 5A packed column (for analyses of H$_2$, O$_2$, and N$_2$). The carbon-based material balance was greater than 95% for all examinations.

A DC high-voltage power supply was used to generate the electric field. The input dark current was changed as a controlling parameter. The impressed voltage depended on characteristics of the catalyst or the reaction conditions. The impressed voltage profile was measured using an oscilloscope and a voltage probe connected to the reactor, as depicted in Fig. 1.

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La$_2$O$_3$ and Sr doped La$_2$O$_3$ (Sr-La$_2$O$_3$) catalysts were prepared using a citric acid method. Precursors La(NO$_3$)$_3$·6H$_2$O and Sr(NO$_3$)$_2$ nitrates were dissolved into distilled water with subsequent addition of an aqueous solution of ethylene glycol and citric acid. After heating at 353 K in a water bath for 18 h, the solution was evaporated completely. Then, the obtained complex was decomposed at 673 K for 2 h using a muffle furnace, with subsequent calcination at 1123 K for 10 h with air flow in a quartz tube reactor. The Sr/La molar ratios of Sr-La$_2$O$_3$ catalysts were 1/20, 1/50, 1/200, 1/500, 1/2000 and 1/5000. Specific surface areas of catalysts were measured using N$_2$ adsorption with BET method (AUTOSORB-1; Quantachrome Instruments). The BET surface areas of Sr-La$_2$O$_3$ (Sr/La = 1/20, 1/50, 1/200, 1/500, 1/2000, or 0) were, respectively, 0.55, 2.46, 3.44, 1.09, 0.85, 1.18 or 2.33 m$^2$ g$^{-1}$. Crystalline structures of these catalysts were characterized by XRD measurement (RINT-2000; Rigaku Corp.) operating at 40 kV and 20 mA using CuK$_\alpha$ radiation filtered by nickel. Each XRD pattern of Sr-La$_2$O$_3$ was attributable to the structure of La$_2$O$_3$, so the doped strontium-ion was introduced and dispersed in the La$_2$O$_3$ structure for these catalysts.

To evaluate electrical properties of catalysts, we measured electrical conductivities of these catalysts using an alternate current (AC) impedance measurement. For the measurement, the catalyst powder was suspended in iso-propanol and crushed into fine particles using a ball-mill (P-6, 200 rpm, 30 min, 3 cycles; Fritsch GmbH). After evaporation of iso-propanol, the powder was pressed at 90 kN for 30 min to produce a disc. The disc was calcined in air at 1473 K for 24 h. For attaching an electrode to the disc, Au paste was dipped on the disc surface and the disc was calcined at 1173 K for 10 min. Electrical conductivities were measured using an impedance analyzer with a potentiostat (IM6eX, Zahner-elektrik GmbH & Co. KG) in Ar atmosphere from 573 K to 973 K. The impedance was measured between 10 mHz and 3 MHz. Bulk conductivity was obtained from measurement of the Nyquist plot using an equivalent circuit as shown in Fig. 2. The equivalent circuit applied the ALS model [21] consisting of a bulk, a grain, and an electrode boundary. We evaluated the catalyst bed temperature using Planck’s formula by emission spectra.

### III. RESULTS

#### A. Screening Tests of Suitable Catalyst in the Electric Field

First, we examined catalytic activities of various catalysts for OCM assisted by a dark current in an electric field. Results are presented in Table I. Rare-earth oxides, especially La$_2$O$_3$, have been reported as effective catalysts for the OCM reaction [2, 4, 7, 8]. However, the dark current was not applicable on some rare-earth oxide catalysts except CeO$_2$ and Gd$_2$O$_3$, as shown in Table I. A spark discharge was generated. Then high CO and C$_2$H$_2$ selectivity were observed for
these rare-earth oxides. Deactivation of catalytic activity was observed because of a large amount of carbon deposit. Our previous research showed that semiconductor catalysts, especially CeO$_2$, which had oxygen-ion conductivity, were effective for applying the electric field. The electric field was applicable on CeO$_2$ and Fe$_2$O$_3$, which had high redox (Ce$^{3+}$/Ce$^{4+}$ and Fe$^{2+}$/Fe$^{3+}$) ability. However, C$_2$ selectivities on CeO$_2$ and Fe$_2$O$_3$ were very low, and formation of much CO$_2$ was observed because of the high combustion activities of CeO$_2$ and Fe$_2$O$_3$ catalyst. We also investigated the catalytic activity of metal-doped La$_2$O$_3$ (M-La$_2$O$_3$) catalysts to achieve high electrical conductivity for applying the electric field. M-La$_2$O$_3$ was also reported as an effective catalyst for the OCM reaction [3, 22], Mg, Ca, Sr, Ba, Y or Zr (5 mol%) was doped into La$_2$O$_3$ as a dopant. As shown in Table I, the electric field was not applicable on Mg-La$_2$O$_3$, Y-La$_2$O$_3$ or Zr-La$_2$O$_3$ catalyst because of the formation of spark discharge (i.e. plasma). Results suggest that these metals (i.e., Mg, Y, and Zr) were not doped into La$_2$O$_3$ and that they did not work as a promoter for ion conduction. The catalytic activity on Sr-La$_2$O$_3$ in the electric field was the highest among these catalysts. Therefore, we chose Sr-La$_2$O$_3$ in further investigations as the best catalyst.

B. Effect of Sr/La Molar Ratio on Sr-La$_2$O$_3$ Catalyst for Applying the Dark Current in an Electric Field

As described above, although the dark current was not applicable on La$_2$O$_3$ catalyst and spark discharge generated, doping Sr into La$_2$O$_3$ enabled stable application of the dark current to the catalyst bed. To evaluate the effect of doped Sr-ion in the Sr-La$_2$O$_3$ on the activity in the electric field, we examined the OCM reaction in the electric field on Sr-La$_2$O$_3$ catalysts which had various Sr/La molar ratios. Results are shown in Fig. 3. The dark current was applicable on Sr-La$_2$O$_3$ catalyst of which the Sr/La molar ratio was greater than 1/200, and spark discharge generated on Sr-La$_2$O$_3$ catalyst of which the Sr/La molar ratio was less than 1/500. Therefore, the amount of doped Sr-ion in Sr-La$_2$O$_3$ was an important factor for applying the dark current. The catalytic OCM reaction, assisted by the dark current (i.e., over catalysts of Sr/La=1/200 and 1/20), showed higher C$_2$ selectivity (C$_2$H$_4$ and C$_2$H$_6$) selectivity and no formation of C$_2$H$_2$. However, plasma OCM reaction proceeded over the catalysts of Sr/La=1/2000 and 0, showing low C$_2$H$_4$/C$_2$H$_6$ selectivity and much C$_2$H$_2$ formation. Reportedly, doping Sr cation into oxide

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Catalytic Activity with 3.0 MA of Dark Current in the Electric Field on Various Catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>Voltage / V</td>
</tr>
<tr>
<td>Blank Discharge</td>
<td>13.7</td>
</tr>
<tr>
<td>La$_2$O$_3$ Discharge</td>
<td>4.9</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>700</td>
</tr>
<tr>
<td>Nd$_2$O$_3$</td>
<td>Discharge</td>
</tr>
<tr>
<td>Sm$_2$O$_3$</td>
<td>Discharge</td>
</tr>
<tr>
<td>Eu$_2$O$_3$</td>
<td>Discharge</td>
</tr>
<tr>
<td>Gd$_2$O$_3$</td>
<td>800</td>
</tr>
<tr>
<td>Dy$_2$O$_3$</td>
<td>Discharge</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>Discharge</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>500</td>
</tr>
<tr>
<td>Mg-La$_2$O$_3$</td>
<td>Discharge</td>
</tr>
<tr>
<td>Ca-La$_2$O$_3$</td>
<td>1100</td>
</tr>
<tr>
<td>Sr-La$_2$O$_3$</td>
<td>900</td>
</tr>
<tr>
<td>Ba-La$_2$O$_3$</td>
<td>900</td>
</tr>
<tr>
<td>Y-La$_2$O$_3$</td>
<td>Discharge</td>
</tr>
<tr>
<td>Zr-La$_2$O$_3$</td>
<td>Discharge</td>
</tr>
</tbody>
</table>

Fig. 3. Catalytic activities and selectivities to products over various Sr-La$_2$O$_3$ catalysts (Sr/La = 0, 1/2000, 1/200, 1/20).
increased the electrical conductivity [23, 24]. Therefore, we measured electrical conductivities of various Sr-La$_2$O$_3$ catalysts using alternate current (AC) impedance measurement. Results are shown in Fig. 4. The vertical axis shows a common logarithm of the electrical conductivity. The electrical conductivity increased concomitantly with increasing Sr/La molar ratio. Stable dark current was applicable over Sr-La$_2$O$_3$ catalysts of Sr/La=1/200 and 1/20. Results show that the electrical conductivity of the catalyst is an important factor for applying the electric field.

We considered the Kröger–Vink formula for the Sr-La$_2$O$_3$ catalyst. The formulae and electroneutrality conditions are shown in Eqs. (2) and (3).

\[ \text{SrO} = \text{SrLa}^+ + \text{O}_2^- + \frac{1}{2} \text{VO}^{••} \quad ([\text{VO}^{••}] = 2[\text{SrLa}^+]) \]  
(2)

\[ \text{SrO} + \frac{1}{4} \text{O}_2 = \text{SrLa}^+ + \frac{3}{2} \text{O}_2^- + \text{h}^{•} \quad ([\text{h}^{•}] = [\text{SrLa}^+]) \]  
(3)

These formulae show that a doped Sr-ion generates half of an oxygen-ion vacancy or an electron–hole. Therefore, the electrical conduction carrier over the catalyst was an oxygen-ion vacancy or an electron–hole acceptor. The amount of the oxygen-ion vacancy or electron–hole was important for applying the dark current in the electric field.

C. Role of the Dark Current to Catalytic Activity

In the section above, we described that Sr-doped La$_2$O$_3$ catalyst, which had Sr/La ratio of 1/200 or higher, showed high catalytic activity for OCM in the electric field. We examined the OCM reaction in various experimental conditions using the Sr-La$_2$O$_3$ catalyst of Sr/La=1/20 and evaluated the effect of the dark current in the electric field on the catalytic activity. Results showed that CH$_4$ conversion is proportional to the contact time in the electric field as well as that in the conventional reaction and that selectivity to C2 hydrocarbon was almost constant under these conditions. However, dependencies of the gap of electrodes and reactor tube diameter in the electric field were not similar to that in the conventional reaction. CH$_4$ conversion increased concomitantly with increasing gap of the electrodes under the same W/F. For the same catalyst bed height, CH$_4$ conversion and selectivity to products showed similar values in various W/Fs. These trends in the electric field were not observed in the conventional catalytic reaction by heat. The catalytic activity is not affected by the aspect ratio of the catalyst bed (i.e. weight and width of the catalyst bed) but by the contact time (GHSV: h$^{-1}$ or W/F: g-cat h mol$^{-1}$) in the conventional catalytic system. On the other hand, the catalytic activity in the present system is affected by the aspect ratio even at the same catalyst amount and gas velocity.

Based on these results, a new concept for the contact time was defined. Contact time between the feed gas and the catalyst activated by the electric field, was defined as an effective contact time (ECT: as shown in Eq. (4)).

\[ \text{ECT (mm min mmol}^{-1}) = \frac{\text{Gap distance (mm)}}{\text{Feed flow rate (mmol min}^{-1})} \]  
(4)

The ECT dependency on each result is shown in Fig. 5. As described above, CH$_4$ conversion was proportional to the feed flow rate and the gap distance of electrodes, and the catalyst between two electrodes was activated by the electric field.

We examined the effect of input current on the catalytic activity in the electric field to discuss the influence of the electron–hole in the catalyst because the electron–hole is expected to be an active site for oxidative coupling of methane [25]. Results are presented in Table II. Increasing the input current provided the increase of CH$_4$ conversion, CO, and CO$_2$ selectivity, in addition to the decrease of C2 (C$_2$H$_4$, C$_2$H$_6$) selectivity. This result implied that the increase of the input current promoted the sequential oxidation from C2 to CO and CO$_2$. Therefore, we also examined the effect of input current at higher gas velocity of W/F=1.6 g h mol$^{-1}$ (i.e.
CH4/O2/Ar = 50/10/200 mL min⁻¹ in the electric field to prevent sequential oxidation. Results show that the C2 selectivity increased at higher gas velocity, as shown in Table II.

To discuss the temperature in the catalyst bed, we measured the maximum temperature using emission spectra. The method using the Planck radiation is shown in elsewhere [20]. The catalyst bed temperature approached temperatures higher than 1200 K, as shown in Table II, because of the exothermic reaction (OCM). We calculated the increase of the temperature caused by the exothermic reaction and sensible heat of the inlet gas from the maximum temperature. About half of the heat was derived from the exothermic heat of OCM. The rest was derived from the Joule heat generated by electrical conduction. In our previous work [20], catalytic activities in the present system and conventional catalytic system were compared using the same catalyst. Even at a temperature as high as 1273 K, the conversion of methane/oxygen and the selectivity to C2 hydrocarbon were lower than those in the present system. So present system enabled high methane conversion thanks to the promotion effect by the dark current, and suppressed sequential oxidation of C2 products to CO/CO₂ due to the low external temperature.

D. Effect of CH₄/O₂ Molar Ratio in the Feed Gas

We examined the OCM reaction using a dark current in the electric field at various CH₄/O₂ molar ratios in feed gases to prevent sequential oxidation in gas phase. Results are shown in Fig. 6. Increased CH₄ partial pressure in feed gases provided increased C2 selectivity and decreased CO₂ selectivity. Selectivity to CO was almost constant for all CH₄/O₂ molar ratios. The highest C2 selectivity of 59% was observed at CH₄/O₂ ratio=10. We infer that the catalytic OCM reaction in the electric field at low external temperature enables high C2 yield. This system with the electric field is applicable to various other reactions.

IV. CONCLUSION

We examined the OCM reaction with a dark current in an electric field in various experimental conditions. Then we measured the electrical conductivity of the catalyst. Results show that the electric field activated the catalyst located between electrodes, and that the electrical conductivity of the catalyst is an important factor for applying the dark current in the electric field. High selectivity and conversion was obtained using the catalytic OCM reaction assisted by a dark current in the electric field at low external temperature.

REFERENCES


