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Catalytic Oxidative Coupling of Methane Assisted by Electric Power over a Semiconductor Catalyst

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Oxidative coupling of methane (OCM) on La_2O_3 semiconductor catalysts at 423 K external temperature was investigated. DC power supplied from two electrodes in a catalyst bed enabled stable and selective production of C_2H_6 and C_2H_4 over Sr–La_2O_3 (Sr/La = 1/200 and 1/20), but plasma reactions proceeded over other catalysts. The electrical conductivity of the semiconductor catalyst was important for controlling this reaction. A high yield of C2 (49% selectivity, 51.3% O_2 conversion) was obtained using 2.7 W of electricity at a lower external temperature (423 K).

Catalytic oxidative coupling of methane (OCM) (eq 1) has received considerable attention because highly valuable C2 hydrocarbons, especially ethylene, are producible from the following one-pass reaction.

$$CH_4 + 1/2O_2 \rightarrow 1/2C_2H_4 + H_2O \tag{1}$$

This reaction has been investigated[1–16] for three decades. The active center of the OCM is known to be active oxygen species on metal oxide catalysts. The rate-determining step in the OCM reaction is CH_3• formation by H abstraction from CH_4 ($E_a = 228\,kJ\,mol^{-1}$ with no catalyst,[14] $109\,kJ\,mol^{-1}$ on Li/MgO catalyst,[4] $212\,kJ\,mol^{-1}$ on $Mn/Na_2WO_4/SiO_2$ catalyst,[15] and $160–180\,kJ\,mol^{-1}$ on La-based catalysts[16]). CH_4 activation on these oxide catalysts necessitates high temperatures over 973 K because of the stable structure of CH_4 and high CH_3–H bond dissociation energy. Coupling of CH_3• in gas phase generates C_2H_6. Although the CH_3• formation reaction requires high activation energy, the activation energy for CH_3• coupling is almost zero.[17] The formation of C_2H_6 by sequential dehydrogenation produces C_2H_4. In addition to the C2 production, CO and CO_2 are generated by both gas phase and catalytic reactions (parallel oxidation of methane and sequential oxidation of C2 compounds). To suppress the successive oxidation of C2 to CO and CO_2, low-temperature conditions are favorable for selective OCM because OCM is an exothermic reaction.

Therefore, nonconventional processes at lower gas-phase temperature have been investigated.[18–20] One example is non-oxidative coupling in low energy pulse (LEP) discharge, as examined by Kado et al.[18,19] In this process, CH_4 is decomposed using a nonequilibrium plasma generated between two electrodes. They reported that C2 production from CH_4 occurred with no catalyst, even at ambient temperature with LEP discharge. However, the produced C2 includes a large amount of C_2H_2, making it unattractive as a chemical feedstock. Furthermore, a great deal of carbon deposition causes a short-circuit between electrodes. CH_4 was decomposed to C or CH, which was a precursor of C_2H_2 formation or carbon deposition.

On the other hand, we have found that catalytic reactions in an electric field enable low-temperature hydrogen production by steam reforming of methane.[21,22] The application of electric field to the semiconductor catalyst promoted dissociation of methane to produce hydrogen at temperature as low as 473 K. Based on this background, we tried to utilize this system for simultaneous C–H bond activation and C–C bond formation.

In this work, we conducted low-temperature methane oxidation to produce C_2H_6 or C_2H_4 using a semiconductor OCM catalyst with electrical power (E-OCM). We applied La_2O_3 and Sr–La_2O_3 catalysts; these catalysts are good candidates for E-OCM because these catalysts have a stable structure and semiconductivity. In addition, Sr–La_2O_3 catalyst (Sr/La = 1/50–1/20) is well known as a good catalyst for conventional catalytic OCM.[6–9,16] Moreover, Borchert et al.[9] suggested that doping Sr into La_2O_3 enhanced electrical conductivity of La_2O_3. Therefore, we prepared various Sr–La_2O_3 catalysts with ratios of Sr/La = 1/20, 1/200, and 1/2000.

Using a citric acid method, we prepared La_2O_3 and Sr-doped La_2O_3 (Sr–La_2O_3). Precursors $La(NO_3)_3 \cdot 6H_2O$ and $Sr(NO_3)_2$ 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 calcined at 673 K for 2 h using a muffle furnace, with subsequent calcination at 1123 K for 10 h with air flow.

Catalytic activity tests assisted by electric power were performed in a fixed bed reactor that included a quartz tube (4 mm i.d.). Then the catalyst was charged in it, as portrayed in Figure 1. A thermocouple was installed in the side of the catalyst bed for controlling the furnace temperature. Two stainless steel electrodes (2 mm o.d.) were inserted from each end of the catalyst bed in the quartz tube reactor. A DC power

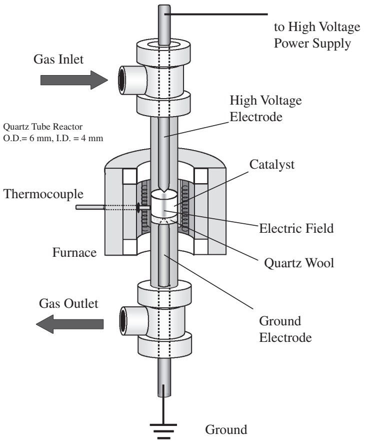

Figure 1. Reaction apparatus.

Table 1. Oxidative coupling of methane over various catalysts with/without the electric field[a]

		External Temp /K	BET S.A. $/m^2\,g^{-1}$	CH_4 Conv. /%	O_2 Conv. /%	C_2H_6 Sel. /%	C_2H_4 Sel. /%	C_2H_2 Sel. /%	CO Sel. /%	CO_2 Sel. /%
La_2O_3	Plasma (2800 V)	423	2.3	6.4	15.7	11.0	5.1	5.8	43.9	34.3
(1/2000-Sr)–La_2O_3	Plasma (3200 V)	423	0.9	6.7	29.5	8.1	3.9	8.8	43.9	35.2
(1/200-Sr)–La_2O_3	E-OCM (900 V)	423	3.4	11.5	70.4	23.8	10.4	0.0	18.8	46.2
(1/20-Sr)–La_2O_3	E-OCM (900 V)	423	0.6	8.9	51.3	33.5	15.5	0.0	15.7	34.9
	External heating	1273		7.4	49.8	27.6	18.0	0.0	15.0	39.3

[a]Reaction conditions: $CH_4/O_2/Ar = 25/5/100\,mL\,min^{-1}$; furnace temperature 423 K; input current 3 mA; catalyst loading 200 mg; $W/F = 3.2$ g-cat. h mol^{-1}.

supply was used to supply current to the catalyst bed with control of the input current at 3 mA. The impressed voltage depended on the semiconductivity of the catalyst. The reaction conditions and the values were between 900 and 3200 V. Reactant feed gas conditions were $CH_4/O_2/Ar = 5/1/20$; W/F was 1.3–3.2 g-cat. h mol^{-1}. Water in the product was removed in a cold trap at the reactor outlet. The dried gas was analyzed using a GC-FID with Porapak N packed column after methanation by Ru/Al_2O_3 catalyst (for analyses of CH_4, CO, CO_2, C_2H_2, C_2H_4, and C_2H_6) and a GC-TCD with molecular sieve 5A packed column (for analyses of H_2 and O_2). The carbon-based material balance was higher than 95% for all experiments. Catalytic activity tests without electric power were also conducted using the same apparatus.

Specific surface areas of catalysts were measured by N_2 adsorption and calculated using the BET method (Autosorb-1; Quantachrome Instruments). Their values were $2.3\,m^2\,g^{-1}$ for La_2O_3, $0.9\,m^2\,g^{-1}$ for Sr–La_2O_3 (Sr/La = 1/2000), $3.4\,m^2\,g^{-1}$ for Sr–La_2O_3 (Sr/La = 1/200), and $0.6\,m^2\,g^{-1}$ for Sr–La_2O_3 (Sr/La = 1/20).

These catalyst structures were characterized using XRD measurements (RINT-2000; Rigaku Corp.) operating at 40 kV and 20 mA, with Cu Kα radiation filtered by Ni. Only La_2O_3 phase was observed for all these catalysts. Therefore, it was surmised that small particles of SrO were dissolved in La_2O_3 structure in the case of Sr–La_2O_3.

Electrical conductivities of catalysts were measured using two-electrode AC impedance (IM6; Zahner-elektrik GmbH & Co. KG). Data for Nyquist and Bode plots were obtained in Ar atmosphere at 573–973 K. Bulk conductivities of catalysts were calculated by decomposing the plots into bulk, grain, and electrode components.

First, we investigated catalytic activities of La_2O_3 or Sr–La_2O_3 (Sr/La = 1/2000, 1/200, and 1/20) catalysts for OCM in DC supply (3 mA) at a constant external temperature of 423 K controlled by outer furnace. These catalysts were known as effective catalysts for catalytic OCM reactions.[6–9,16] We performed the reactions without a DC supply on these catalysts as controls. The impressed voltage was 2800 V for La_2O_3, 3200 V for Sr–La_2O_3 (Sr/La = 1/2000), and 900 V for Sr–La_2O_3 (Sr/La = 1/20). Table 1 presents catalytic activities on these catalysts with and without a DC supply at similar methane conversion. For La_2O_3 and Sr–La_2O_3 (Sr/La = 1/2000) catalysts with DC supply, plasma formation was observed as described by Kado et al.:[18,19] with high C_2H_2 selectivity and much carbon deposition. On the other hand, the Sr–La_2O_3 (Sr/La = 1/200 and 1/20) catalysts exhibited distinctly different activity from those of La_2O_3 and Sr–La_2O_3 (Sr/La = 1/2000) catalysts with a DC supply. On Sr–La_2O_3 (Sr/La = 1/20) catalyst, stable electric field was achieved, C_2H_6 and C_2H_4 were produced with the selectivity of 49% for these two products. Higher methane conversion (8.9%) and lower CO_2 selectivity (34.9%) with electric power were observed than the results at 1273 K without electric power: i.e., conventional catalytic reaction (methane conversion: 7.4%, CO_2 selectivity 39.3%). In this case, no production of C_2H_2 was observed which could be produced solely by a plasma reaction. In the case of E-OCM over Sr–La_2O_3 (Sr/La = 1/20) catalyst, the estimated inner temperature of the catalyst bed by the observation of Planck radiation (Figure 2) was about 1273 K due to the heat supply by the exothermic reaction and the Joule heat by electric power. The inner temperature of the catalyst bed was stable for long time course due to the balance among exothermic OCM reaction, Joule heat, and the radiation of heat from the reactor. From these results, this system can promote OCM reaction selectively with suppressing sequential gas-phase oxidation to CO, CO_2.

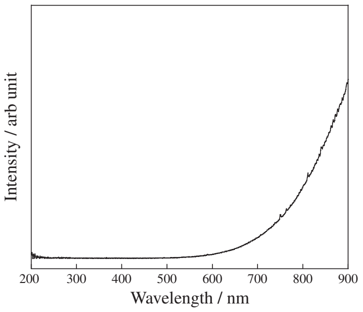

Figure 2. Planck radiation of the electric field on Sr–La_2O_3 (Sr/La = 1/20).

As described above, the reaction field type depended on the amount of Sr doping into La_2O_3 catalyst for both plasma reactions and stable catalytic reactions by E-OCM. To investigate the reaction field type and electrical conductivities of catalysts, electrical conductivities of La_2O_3 and Sr–La_2O_3 (Sr/La = 1/2000, 1/200, and 1/20) catalysts were measured using AC impedance. Figure 3 portrays the electrical conductivities of La_2O_3 and Sr–La_2O_3 (Sr/La = 1/2000, 1/200, and 1/20). Detailed results for the Nyquist and Bode plots for these catalysts are shown in Supporting Information.[23] The Sr–La_2O_3 (Sr/La = 1/200 and 1/20), which brought a stable catalytic reaction by E-OCM, exhibited higher electrical conductivity than either La_2O_3 or Sr–La_2O_3 (Sr/La = 1/2000), which caused a pulsed plasma reaction. The electrical conductivities increased concomitantly with increasing Sr doping into La_2O_3. Therefore,

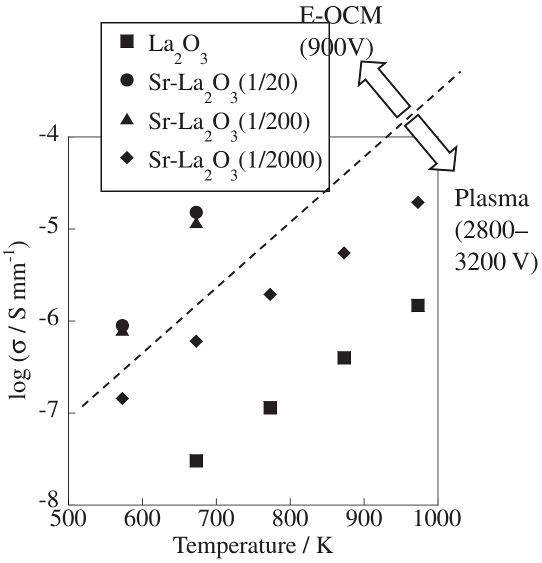

Figure 3. Electrical conductivity for La_2O_3 and $Sr–La_2O_3$ (Sr/La = 1/2000, 1/200, and 1/20) at various temperatures.

the electrical conductivity of catalysts played an important role for effective utilization of the electrical power to produce C_2H_6 and C_2H_4 by E-OCM.

On $Sr–La_2O_3$ (Sr/La = 1/20) catalysts with the electric field, 2.7 W electrical power was applied to the catalyst bed (3 mA, 900 V) in the steady-state reaction. This electrical power of 2.7 W was used for promoting the reaction and raising the temperature simultaneously. Detailed analyses for the role of support and electricity will be investigated in future.

We performed OCM with DC supply on La_2O_3 or $Sr–La_2O_3$ (Sr/La = 1/2000, 1/200, and 1/20) catalysts. For La_2O_3 or $Sr–La_2O_3$ (Sr/La = 1/2000), C_2H_2 was generated by the plasma reaction. For $Sr–La_2O_3$ (Sr/La = 1/200 and 1/20), C_2H_6 and C_2H_4 were generated selectively by the E-OCM reaction. Electrical conductivity of the catalysts was important for achieving stable E-OCM reaction.

Oxidative coupling of methane in an electric field (E-OCM) over $Sr–La_2O_3$ catalyst (Sr/La = 1/20) supports a high yield of C2 hydrocarbon at low external temperature (423 K).

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