Electric Field and Mobile Oxygen Promote Low-Temperature Oxidative Coupling of Methane over La$_{1-x}$Ca$_x$AlO$_3$$_{3-\delta}$ Perovskite Catalysts

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Supporting Information

ABSTRACT: Oxidative coupling of methane (OCM) over La$_{1-x}$M$_x$AlO$_3$$_{3-\delta}$ (M = Ca, Sr, Ba; x = 0, 0.1, 0.2, 0.3) in an electric field at low temperature (423 K) was investigated. Among the tested catalysts, the La$_{0.7}$Ca$_{0.3}$AlO$_3$$_{3-\delta}$ catalyst showed the highest performance in terms of C$_2$H$_6$ + C$_2$H$_4$ yield (11.1%). Surface mobile oxygen species (O$_2$$_{5-}$ or O$^-$), which were considered as active oxygen species for the OCM reaction, increased with increasing Ca doping amount, and thereby the La$_{0.7}$Ca$_{0.3}$AlO$_3$$_{3-\delta}$ catalyst showed the best catalytic activity.

INTRODUCTION

Oxidative coupling of methane (OCM) is a reaction to produce C$_2$ hydrocarbons from methane and oxygen directly. It has been attracting lots of attention and has been investigated from the 1980s because of the need for technical development to convert natural gas to added value chemicals.1–3 Even though the OCM reaction is exothermic thermodynamically, it requires a high reaction temperature over 900 K because of high energy required for dissociation of the C–H bond in methane.4 At such high temperature, C$_2$ hydrocarbons tend to be oxidized to CO and CO$_2$, resulting in a drastically decreased C$_2$ selectivity. To prevent the undesirable nonselective reactions, we conducted the OCM reaction in a low-temperature region by applying an electric field. Under constant current to the catalyst-bed, the OCM reaction proceeded at the low reaction temperature of 423 K over Ce$_2$(WO$_4$)$_2$/CeO$_2$ catalyst.5–9

Many researchers have reported that the active oxygen species on the catalyst is an active site of the OCM reaction.1,10–13 These oxygen species (e.g., O$_2$$_{5-}$, O$^-$, O$_2$$_{2-}$, and/or O$^{\cdot-}$) abstract hydrogen atom from methane.6 Perovskite-type oxide materials are known to generate such oxygen species with high mobility in low-temperature regions relatively.14 Especially, among many kinds of perovskite-type oxides, LaAlO$_3$ shows high OCM activity.6,10,15,16 By doping alkali or alkali-earth metal cations, which have strong basic nature, high C$_2$ selectivity can be obtained.17,18 In addition, substitution of La$^{3+}$ cation by such cations resulted in increase of oxygen deficiency in the lattice structure and this, in turn, contributed to production of O$^-$ and O$_2$$_{5-}$ type oxygen species.19,20

Herein, we investigated catalytic activity of OCM in the electric field at the low temperature of 423 K over alkali-earth metal cations (Ca, Sr, and Ba)-substituted LaAlO$_3$ catalysts. The reaction mechanism and effects of substituted alkali-earth metal cations on its structure, electronic state, and OCM activity were also investigated.

RESULTS AND DISCUSSION

First, we investigated the catalytic OCM activity of La$_{0.7}$Ca$_{0.3}$AlO$_3$$_{3-\delta}$ at 423 K in the electric field, and the results are presented in Figure 1 and Table S1. The results show that La$_{0.7}$Ca$_{0.3}$AlO$_3$$_{3-\delta}$, La$_{0.7}$Sr$_{0.3}$AlO$_3$$_{3-\delta}$ and La$_{0.7}$Ba$_{0.3}$AlO$_3$$_{3-\delta}$ showed OCM activity at the low temperature of 423 K in the electric field (imposed current 3.0 mA). Among the tested catalysts, La$_{0.7}$Ca$_{0.3}$AlO$_3$$_{3-\delta}$ showed the highest C$_2$H$_6$ + C$_2$H$_4$ yield and selectivity. It is noteworthy that the La$_{0.7}$Ca$_{0.3}$AlO$_3$$_{3-\delta}$ catalyst showed higher C$_2$H$_6$ + C$_2$H$_4$ yield than that of the previously reported catalysts, thanks to its redox property (details are discussed in following section). Moreover, the La$_{0.7}$Ca$_{0.3}$AlO$_3$$_{3-\delta}$ catalyst showed stable activity for at least 180 min (Figure S1) without significant structural deformation and coke formation (Figures S2 and S3). From these results, La$_{0.7}$Ca$_{0.3}$AlO$_3$$_{3-\delta}$ was the most suitable catalyst for the OCM reaction.
among the La−M−Al−O perovskite catalysts in the OCM reaction under electric field.

The effect of electric field on the activity of La0.7Ca0.3AlO3−δ catalyst was investigated by comparing the activity with or without the electric field. Results are shown in Figure 2 and Table S2. As shown in Figure 2, with the aid of electric field, CH4 conversion, O2 conversion, and C2H6 + C2H4 yield for the reaction in the electric field were extremely high at low temperature, whereas no OCM activity was found without the electric field. On the other hand, in the reaction without the electric field, C2H6 + C2H4 yield steeply increased with temperature above 800 K. It is well known that perovskite oxide releases its lattice oxygen at high temperature (i.e., above 800 K for La0.7Ca0.3AlO3−δ), and it contributed to hydrocarbon conversion by the Mars van Krevelen mechanism.21−24 The isotopic oxygen exchange tests revealed that the lattice oxygen was exchanged by gas phase molecular oxygen at 473 K with the electric field and at above 800 K without the electric field (see the Supporting Information, Figures S4 and S5). The temperature of the catalyst was measured by a thermocouple, and the effect of Joule heat by the electric field on the catalytic activity was negligible. From these results, it is considered that applying electric field to La0.7Ca0.3AlO3−δ promotes the release of its lattice oxygen even at low temperature below 700 K, and thereby the OCM reaction takes place.

In addition, as shown in Table S1, field intensity of the applied electric field was ca. 150 V mm−1, which is much lower than that of a plasma-catalyst hybrid system.25 Moreover, the present electrocatalytic system can proceed the OCM reaction at lower temperature (<700 K) than that of a high-temperature electrochemical reaction using a SOFC (solid oxide fuel cell) system (>873 K),14,26 although the field intensity was higher than that of the SOFC system (<30 V mm−1). Therefore, the present reaction system, catalytic reaction in an electric field, is a mild and efficient low-temperature electrocatalytic OCM.

To clarify effects of Ca doping amount in LaAlO3 on its structure and OCM activity, La1−xCa0.3AlO3−δ catalysts with various Ca doping amount (x = 0, 0.1, 0.2, and 0.3) were prepared and evaluated. Details of the structural characterizations are described in the Supporting Information (Figures S6, S7, and Table S3). Figure 3 and Table S4 show results of activity tests over La1−xCa0.3AlO3−δ catalysts in the electric field. O2 partial pressure decreased from 15% to 5% for comparison of these activities and selectivity precisely. In the case of LaAlO3 catalyst, spark discharge was observed due to its low electron, hole, and/or ion conductivity,27 and no products were formed. As the Ca doping amount increased, CH4 and O2 conversions and C2H6 + C2H4 yield increased. Reportedly, the amount of lattice oxygen defect increases by substituting cations with different oxidation numbers in perovskite structures, which promotes redox reaction using lattice oxygen through the Mars van Krevelen mechanism.21−24 In the present catalytic system, the lattice oxygen contributes to methane activation and C2 product formation. Therefore, it is considered that Ca doping to LaAlO3 contributed to increase the amount of lattice oxygen defects, and thereby the conversions and C2H6 + C2H4 yield increased as Ca doping amount increased.

X-ray photoelectron spectroscopy (XPS) measurements were conducted to investigate the difference in electronic states of lattice or surface oxygen over La1−xCa0.3AlO3−δ catalysts. Figure S8 shows O 1s spectra of La1−xCa0.3AlO3−δ catalysts. Each O 1s spectrum could be deconvoluted to three peaks: the peaks at around 529, 531, and 532 eV were assignable to Olat (lattice oxygen; O2−), O1 (surface or mobile oxygen; O2− and O−), and H2O(ad) (adsorbed H2O), respectively.10,16,28−30 The mobile oxygen (O1) ratio was calculated by the following eq 1.

$$\text{mobile oxygen O1 ratio (%) = } \frac{Q_1}{Q_{tot} - Q_{lat}} \times 100$$  

(1)
Tables 1 and S5 present the result of O 1s XPS measurements. From Table 1, the O₈ ratio increases by increasing the amount of Ca doping. Therefore, we deduced the relationship between C₂H₆ + C₂H₄ yield and O₈ ratio as shown in Figure 4. A linear correlation was found between the O₈ ratio and C₂H₆ + C₂H₄ yield (and CH₄ conversion), suggesting that the O₈ ratio over La₁₋ₓCaₓAlO₃₋δ catalyst plays an important role in the OCM reaction. It was reported that electrophilic oxygen species (e.g., O⁻), which was formed by reaction of O₂ molecule with metal cations or oxygen vacancies over the surface of metal oxide catalysts, contribute homolytic C–H bond dissociation to form methyl radicals. Also, it was reported that Os species (O⁻ and O₂⁻) participate in the redox reaction. From the obtained results and literature, it is considered that O₈ on La₁₋ₓCaₓAlO₃₋δ is the active oxygen species that participates in the OCM reaction as a redox active site via the Mars van Krevelen mechanism. Therefore, the OCM activity improved by Ca doping thanks to increase in the O₈ ratio as increasing the substituting amount of Ca.

To elucidate the reaction pathway on the La₀.⁷Ca₀.₃AlO₃₋δ catalyst in the electric field, the effect of contact time (W/FCH₄) was investigated. O₂ partial pressure was set to 5% to evaluate the product selectivity at the initial stage. Figure 5 and Table S6 present the influence of W/FCH₄ on CH₄ conversion, O₂ conversion, and selectivity of each product. As shown in Figure 5a, CH₄ conversion and O₂ conversion increase as the contact time increases. As shown in Figure 5b, C₂H₆ selectivity decreased gradually as the W/FCH₄ increased, and C₂H₄ selectivity was almost constant in low W/FCH₄ region, and it decreased with further increase in W/FCH₄. On the other hand, C₂H₂ selectivity was almost zero under these conditions, suggesting that C₂H₂ was hardly produced by successive dehydrogenation of C₂H₄. CO and CO₂ were formed even at low W/FCH₄, and CO selectivity increased as the contact time increased, which implies that CO and CO₂ were produced from methane directly (parallel reaction) in low W/FCH₄ region and by oxidation of C₂ products (successive reaction) in high W/FCH₄ region. From these results, the main reaction pathway is suggested as follows: C₂H₆ was formed by OCM reaction over the La₀.⁷Ca₀.₃AlO₃₋δ catalyst at first, and then C₂H₄ was produced by oxidative dehydrogenation of C₂H₆, and finally they were oxidized to CO and CO₂.

In order to investigate the reactivity of C₂ products, the reactant was changed from CH₄ to C₂H₆ or C₂H₄. The results of each catalytic activity test are shown in Table S7. In each case, C₂ hydrocarbons, CH₄, CO, and CO₂ were produced; however C₃+ hydrocarbons were not detected. From Table S6, C₂H₆ conversion was lower than CH₄ conversion, and C₂H₆ was mainly converted to C₂H₄ by oxidative dehydrogenation. Similar to the CH₄ reaction, C₂H₄ selectivity in C₂H₆ or C₂H₄ reaction was also very low. Although main products from C₂H₄ were CO and CO₂, C₂H₄ conversion was low despite the presence of unreacted O₂. Considering the obtained results, the C–H bond of C₂H₆ was selectively dissociated rather than C–C bond dissociation. Also, both dehydrogenation and oxidation of C₂H₄ hardly proceeded in the present system.

![Figure 4](image-url) Relationship between O₈ ratio and OCM activity of La₁₋ₓCaₓAlO₃₋δ catalysts.

![Figure 5](image-url) Effect of W/FCH₄ on activity and selectivity of La₀.⁷Ca₀.₃AlO₃₋δ catalyst: (a) conversions and C₂H₆ + C₂H₄ selectivity, (b) product selectivities.

### Table 1. Surface Oxygen (O₈) Ratio over La₁₋ₓCaₓAlO₃₋δ (x = 0, 0.1, 0.2, 0.3) Catalysts Obtained by O 1s XPS Analysis

| catalyst          | H₂O(ad) | O₈       | Olat | O₈ ratio * (%) |
|-------------------|---------|----------|------|----------------|
| LaAlO₃            | 16.3    | 16.9     | 66.8 | 20.2           |
| La₀.⁹Ca₀.₁AlO₃₋δ | 16.8    | 21.4     | 61.9 | 25.7           |
| La₀.⁸Ca₀.₂AlO₃₋δ | 16.2    | 25.3     | 58.3 | 30.3           |
| La₀.⁷Ca₀.₃AlO₃₋δ | 13.7    | 29.0     | 57.3 | 33.6           |

* O₈ ratio (%) = (O₈/(O₈ + Olat)) × 100.
Scheme 1 shows a possible reaction pathway. Therefore, the high C₃H₆ + C₂H₄ yield was obtained over the La₀.7Ca₀.3AlO₃₋₅ catalyst with the electric field.

**Scheme 1. Possible Reaction Pathway**

![Diagram](image)

**CONCLUSIONS**

In conclusion, OCM has been conducted over various perovskite oxide catalysts in the electric field at low temperature. Applying the electric field facilitated the OCM reaction under low reaction temperature (423 K). The La₀.7Ca₀.3AlO₃₋₅ catalyst showed the highest C₂H₆ + C₂H₄ yield (11.1%) than ever. Surface mobile oxygen species (O₂⁻ or O⁺) on La₁₋ₓCaₓAlO₃₋₅ was considered as active oxygen species for the OCM reaction via the Mars van Krevelen mechanism. The O₂⁻ ratio increased with increasing the amount of Ca doping, and thereby the OCM activity improved. In this catalytic system, oxidative dehydrogenation of C₂H₆ easily proceeds, whereas successive C₂H₄ conversion hardly does, resulting in high C₂H₆ + C₂H₄ yield. La₀.7Ca₀.3AlO₃₋₅ generated effective oxygen species in the electric field, which brought high C₂H₆ + C₂H₄ yield at low reaction temperature of 423 K.

**EXPERIMENTAL SECTION**

**Catalyst Preparation.** Perovskite oxide catalysts (La₁₋ₓMₓAlO₃₋₅ M = Ca, Sr, Ba; x = 0, 0.1, 0.2, 0.3) were prepared by a citric acid complex method according to the reported procedure. First, metal nitrate precursors were prepared by a citric acid complex method according to the reaction temperature of 423 K.

**Activity Tests.** Catalytic activity tests were conducted in a fixed-bed flow type reactor with a quartz tube (6 mm o.d., 4 mm i.d.). Figure S9 shows schematic diagram of the reactor. The catalysts were sieved to 355–500 μm, and 100 mg of it was inserted into the reactor. To impose electric field to the catalyst, two stainless-steel electrodes were inserted to the upper-side and the bottom-side of the catalyst-bed. The constant current of 3.0 mA was imposed to the catalyst bed using a dc power supply. The reactant feed gases were methanen, oxygen, and argon in the ratio of CH₄/O₂/Ar = 25:15:60 (total flow rate 100 SCCM) for catalyst screening test and stability test and CH₄/O₂/Ar = 25:5:70 (total flow rate 100 SCCM) for investigating the effects of W/FCH₄ and Ca-doping amounts. For determining the reactivity of ethane and ethylene, C₂H₆ and C₂H₄ were fed into the reactor instead of methane. The ratio of the feed gas was C₂H₆/C₂H₄ or C₂H₆/O₂/Ar = 25:15:60 (total flow rate 100 SCCM). The product gases were analyzed with a GC-FID (GC-2014s; Shimadzu Corp.) with Porapak N packed column and a handmade methanizer (Ru/Al₂O₃) and a GC-TCD (GC-2014s; Shimadzu Corp.) with molecular sieve 5A packed column. CH₄ conversion, C₂H₆ conversion, and C₂H₄ conversion were calculated by the following formulas.

\[ CH₄ \text{ conversion} = \frac{\text{carbon moles of (C}_2\text{H}_2, \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \text{CO, and CO}_2)}{\text{carbon mole of input CH}_4} \times 100 \]  

\[ O₂ \text{ conversion} = \frac{\text{consumption moles of O}_2}{\text{input moles of O}_2} \times 100 \]  

\[ \text{product yield} = \frac{\text{carbon mole of product}}{\text{carbon mole of input CH}_4} \times 100 \]  

\[ \text{product selectivity} = \frac{\text{product yield}}{\text{CH}_4 \text{ conversion}} \times 100 \]  

\[ C_2H_2 \text{ conversion} = \frac{\text{carbon moles of (C}_2\text{H}_2, \text{C}_2\text{H}_4, \text{CH}_2\text{O, CO, and CO}_2)}{\text{carbon mole of input C}_2\text{H}_6} \times 100 \]  

\[ C_2H_4 \text{ conversion} = \frac{\text{carbon moles of (C}_2\text{H}_2, \text{C}_2\text{H}_4, \text{CH}_2\text{O, CO, and CO}_2)}{\text{carbon mole of input C}_2\text{H}_4} \times 100 \]

**Characterization.** The catalyst structure was characterized by powder X-ray diffraction (SmartLab III; Rigaku Corp.) at 40 kV and 40 mA with Cu Kα radiation and Raman spectroscopy (NRS-4500; Jasco Corp.) with green laser (λ = 538 nm). Transmission electron microscopy (TEM) observations were performed using field emission-transmission electron microscope (JEM2100-F; JEOL Ltd.) operated at 200 kV. The specific surface area of each catalyst was measured by N₂ physisorption at 77 K with the Brunauer–Emmett–Teller method (GeminiVII; Micromeritics Instrument Corp.) after pretreatment at 573 K for 2 h in an Ar atmosphere (Table S8). XPS (VersaProbe2; ULVAC-PHI Inc.) measurements were conducted with an Al Kα X-ray source. The binding energies were referenced to C 1s peak at 284.8 eV. The O¹⁸/O¹⁶ isotopic oxygen exchange tests in the temperature-programmed reaction or isothermal transient reaction were conducted using the fixed-bed continuous flow-type reactor equipped with a quadrupole mass spectrometer (QGA; Hiden Analytical Ltd.). Details are described in the Supporting Information.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00594.
isotopic oxygen exchange test; Raman spectra; O 1s X-ray photoelectron spectra; schematic diagram of the reactor; and effect of input electric power on CH₄ conversion, C₂H₆ + C₂H₄ yield, and C₂H₆ + C₂H₄ selectivity of La₋ₓSrₓCoO₋ₓ₋₄₋₆ catalyst (PDF)

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Notes
The authors declare no competing financial interest.

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