Low-temperature catalytic oxidative coupling of methane in an electric field over a Ce–W–O catalyst system

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We examined oxidative coupling of methane (OCM) over various Ce–W–O catalysts at 423 K in an electric field. Ce₂(WO₄)₃/CeO₂ catalyst showed high OCM activity. In a periodic operation test over Ce₂(WO₄)₃/CeO₂ catalyst, C₂ selectivity exceeded 60% during three redox cycles. However, Ce₂(WO₄)₃/CeO₂ catalyst without the electric field showed low activity, even at 1073 K: CH₄ Conv., 6.0%; C₂ Sel., 2.1%. A synergetic effect between the Ce₂(WO₄)₃ structure and electric field created the reactive oxygen species for selective oxidation of methane. Results of XAFS, in-situ Raman and periodic operation tests demonstrated that OCM occurred as the lattice oxygen in Ce₂(WO₄)₃ (short W–O bonds in distorted WO₄ unit) was consumed. The consumed oxygen was reproduced by a redox mechanism in the electric field.

Natural gas is being discovered in many countries around the world. The United States and China have recently started to extract large amounts of shale gas. Nevertheless, the state of natural gas, especially methane, at room temperature and atmospheric pressures is gaseous. Therefore, it is transported using gas pipelines or LNG systems. Small and medium-sized natural gas fields have difficulty using such methods. Therefore, efficient conversion of methane to valuable chemicals and fuels is necessary for such cases. Methane conversion processes are categorized into two methods: selective oxidation of methane to useful hydrocarbons or oxygenates, and production of syngas by steam reforming, dry reforming, or partial oxidation of methane. We specifically examined direct catalytic methane conversion to C₂ hydrocarbons by oxidative coupling of methane (OCM)¹–⁵. The formula can be described as presented below (eq. 1).

\[ \text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \frac{1}{2}\text{C}_2\text{H}_4 + \text{H}_2\text{O} (\Delta H_{298}^\circ = -140.1 \text{ kJ mol}^{-1}) \] (1)

Because of its stable tetrahedral structure, methane activation requires temperatures higher than 973 K. Furthermore, the reactivity of ethylene is higher than that of methane. Consequently, C₂ selectivity decreases because gas-phase non-selective and sequential oxidation with oxygen to form CO and CO₂ is unavoidable at such high temperatures. Therefore, it is extremely difficult to obtain high C₂ yield with OCM.

To resolve the difficulties described above, we adopted a non-conventional catalytic system, a catalytic reaction in an electric field, in anticipation of methane activation at low temperatures. Results show that various low-temperature catalytic reactions such as methane steam reforming⁶–¹⁰ can proceed in the electric field. We also reported that OCM proceeded at a low temperature (423 K) in the electric field over Sr-La₂O₃ (Sr/La = 1/20) catalyst¹¹,¹². Although the Sr-La₂O₃ catalyst showed high C₂ selectivity (49.0%), CH₄ conversion remained low (8.9%) in the electric field with imposition of 3.0 mA of current. Further catalyst development is necessary for OCM in an electric field at low temperatures.

As described in this paper, we specifically examined Ce–W–O system oxide catalysts, including Keggin-type heteropoly acids (HPAs) as catalysts, for improving OCM activity in the electric field. HPAs are inorganic metal–oxide anion clusters having multi-electronic redox properties¹³–¹⁴. Keggin-type heteropolytungstates are polyoxometalates containing one central heteroatom X surrounded by 12 condensed W–O octahedra to form \[ [XW_{12}O_{40}]^{n^-} \] (X: P (n = 3), Si (n = 4), etc.). Keggin-type HPAs and the substituted Keggin-type HPAs show unique redox and catalytic properties¹⁵–²³. Many studies of the partial oxidation of methane using HPAs have been conducted using these properties of HPAs. J. B. Moffat et al.²⁴–²⁷ reported the partial oxidation of methane.
into CO, HCHO, and CH₃OH (oxidant: O₂ and N₂O) over HPAs/SiO₂, but the conversion of methane was low (approx. 5%, 843 K). Mizuno et al.²⁸–³¹ reported selective partial oxidation of propane with O₂ over Cs₂.5Fe₀.08H₁.26PVMo₁₁O₄₀. The yield of acrylic acid was 13% at 653 K. For the partial oxidation of methane, the conversion of methane was 0.2%; the catalyst showed almost no activity. Mizuno et al. concluded that the order of C–H bond strength is C₃H₈ < C₂H₆ < CH₄ and that the difference in the activity for lower alkane conversions is attributable to the C–H bond strength.

Based on the discussion presented above, we investigated application of the electric field to Ce–W–O system catalysts including HPAs for low-temperature methane conversion. Important findings included the following: 1) 40 wt%TBA-PW₁₂O₄₀/CeO₂ catalyst showed high OCM activity only in the electric field. The structure was changed to Ce₂(WO₄)₃/CeO₂. 2) The Ce₂(WO₄)₃ structure, which functioned as an active site structure for selective oxidation of methane, worked only in an electric field. 3) Short W–O bonds of the distorted WO₄ unit in Ce₂(WO₄)₃ was an active site in the electric field; OCM occurred by a redox mechanism.

Results and Discussion
Activity tests over TBA-HPAs/CeO₂ catalysts. First, catalytic oxidative coupling of methane (OCM) over various Ce–W–O oxide system catalysts including 40 wt%TBA-PW₁₂O₄₀/CeO₂ (TBA: tetrabutylammonium) without an electric field was conducted at 573–1073 K (Supplementary Information Table S1). TBA-PW₁₂O₄₀/CeO₂ catalyst showed low OCM activity (CH₄ Conv., 5.0%; C₂ Sel., 3.5%) without the electric field, even at the high temperatures of 1073 K.

Next, we evaluated the effects of an electric field on OCM activity over various catalysts including TBA-PW₁₂O₄₀/CeO₂ catalyst (Supplementary Information Tables S2 and S3). TBA-PW₁₂O₄₀/CeO₂ catalyst showed high OCM activity (CH₄ Conv., 52.8%; C₂ Sel., 32.0%; C₂ Yield, 16.9% at imposed current 7.0 mA) in the electric field. Bare CeO₂ catalyst showed high CH₄ conversion (28.2%), but CeO₂ contributed to complete oxidation of methane to produce CO₂ with 98% selectivity in the electric field. Results show that the OCM activity of TBA-PW₁₂O₄₀/CeO₂ was derived from the supported TBA-PW₁₂O₄₀. However, bare TBA-PW₁₂O₄₀ was unsuitable for imposing the electric field because of its electric conductivity.

As-made and after-reaction samples were characterized with Raman, XRD, and FT-IR (Supplementary Information Figs S1–S3). As-made samples were attributed to TBA-PW₁₂O₄₀ and CeO₂. After reaction, the peaks corresponding to TBA-PW₁₂O₄₀ disappeared. New peaks, which were attributable to WO₃ and Ce₂(WO₄)₃, appeared. Therefore, it is likely that these oxides contribute to OCM activity.

To confirm the OCM activity for these oxides without an electric field, OCM over TBA-PW₁₂O₄₀/CeO₂ catalyst at 573–1073 K without an electric field was conducted after reaction with an electric field (423 K, 3.0 mA) to form the oxides described above (Supplementary Information Fig S4). With an electric field, TBA-PW₁₂O₄₀/CeO₂ catalyst showed the following: CH₄ Conv., 14.1%; C₂ Sel., 44.4%. After turning off the electric field, CH₄ and O₂ conversion and C₂ selectivity decreased dramatically at 1073 K: CH₄ Conv., 2.1%; C₂ Sel., 5.0%. Results show that the formed oxides can produce reactive oxygen species and activate methane only when an electric field is applied.

Clarification of the active site structure. As described in the section above, the supported TBA-PW₁₂O₄₀ on CeO₂ was converted to Ce₂(WO₄)₃ and WO₃ during OCM with an electric field. The formed oxides might play an important role for OCM with an electric field. Therefore, OCM activities over Ce₂(WO₄)₃/CeO₂, WO₃/CeO₂, Ce₂(WO₄)₃ and WO₃ catalysts were investigated in the electric field. Structures of the supported and the unsupported oxide catalysts were confirmed using Raman and XRD measurements (Fig. 1(a) and Supplementary Information Fig. S5(a)). Results of activity tests over these oxides at 423 K with an electric field are presented in Table 1, which shows that Ce₂(WO₄)₃/CeO₂, WO₃/CeO₂ and Ce₂(WO₄)₃ showed OCM activity, although WO₃...
showed no OCM activity. Actually, Ce2(WO4)3/CeO2 showed the following for Ttc of 649 K: CH4 Conv., 13.6%; C2 Sel., 39.0%. For Ttc of 634 K, WO3/CeO2 showed the following: CH4 Conv., 14.3%; C2 Sel., 32.4%. Also, Ce2(WO4)3 showed the following for Ttc of 659 K: CH4 Conv., 9.7%; C2 Sel.: 41.2%. Additionally, WO3 catalyst showed no OCM activity even at almost the same temperature (around 650 K) or at almost the same input power (around 2.5 W) as the other catalysts (Supplementary Information Tables S4 and S5). Ce2(WO4)3/CeO2 catalyst showed the higher OCM activity than TBA-PW12/CeO2 catalyst at almost the same input power (2.6–2.7 W) (Supplementary Information Table S4).

The structures of Ce2(WO4)3/CeO2, WO3/CeO2, Ce2(WO4)3, and WO3 catalysts before and after reaction with electric field were analyzed using Raman spectroscopy and XRD (Fig. 1(b) and Supplementary Information Fig. S5(b)). As shown in Fig. 1(b), the structures of Ce2(WO4)3/CeO2, Ce2(WO4)3, and WO3 after reaction with the electric field were not markedly different from as-made. However, the spectrum of WO3/CeO2 after reaction with an electric field differed considerably from as-made. The Raman spectrum showed that W species in WO3/CeO2 changed to Ce2(WO4)3 from WO3 after reaction in the electric field. Supplementary Information Fig. S5 (XRD patterns) presents similar results. It is conceivable that the formation of Ce2(WO4)3 proceeded as a solid–solid reaction between CeO2 and WO3 in the reaction with an electric field32. In light of the activity test over WO3/CeO2, one can infer that the Ce2(WO4)3 formed on WO3/CeO2 activated methane and that it showed OCM activity. Therefore, activity tests and characterizations demonstrated that the active site structure for OCM with the electric field was Ce2(WO4)3. Moreover, the active site structure, Ce2(WO4)3, showed stable OCM activity for at least one hour (Supplementary Information Fig. S6).

Contribution of the active site to OCM activity. To elucidate the contribution of the active site to OCM activity, OCM at 573–1073 K over Ce2(WO4)3/CeO2 catalyst was conducted without an electric field. Results of activity tests (573–1073 K) are presented in Table 2. In the reaction at 1073 K without the electric field, the catalyst showed results (CH4 Conv., 6.0%; C2 Sel., 2.1%) that were much lower than those in the reaction with the electric field at external temperature of 423 K (Ttc measured catalyst bed temperature by thermocouple: 649 K): CH4 Conv., 13.6%; C2 Sel., 39.0%. These results demonstrate that Ce2(WO4)3/CeO2 catalyst can produce reactive oxygen species and activate methane only when an electric field is applied.

In the reaction with an electric field, the catalyst bed temperature increased by Joule heating. Therefore, to elucidate the influence of Joule heating on OCM in the gas phase, the temperature dependency of OCM in the electric field was evaluated. Table 3 presents the activities of OCM over Ce2(WO4)3/CeO2 at 423, 673, and 873 K with the electric field (3.0 mA). C2 selectivity and C2 yield decreased in association with increasing temperature. This reduction caused by combustion of C2 species with O2 in gas phase because O2 conversion increased in proportion to increasing temperature. Therefore, OCM in the gas phase is not promoted by Joule heating from the electric field. The effect of Joule heating by an electric field is unimportant in the system. In other words, because the catalyst was able to activate methane at a low gas-phase temperature, C2 selectivity was high in the OCM with the electric field at low temperature. The same trend was obtained in the case of electric power fixing to normalize the electric factor (Supplementary Information Table S6).

### Table 1. Catalytic activities over various oxide catalysts in the electric field. *Feed gas, CH4:O2:Ar = 25:15:60 SCCM; input current, 3.0 mA; catalyst weight, 100 mg; furnace temperature, 423 K.

| Catalysts | Ttc/K | Voltage/KV | CH4 Conv./% | O2 Conv./% | C2 Sel./% | C2 Yield/% | Field intensity/V mm−1 | Faradic number/— |
|-----------|-------|------------|-------------|-----------|-----------|------------|----------------|-------------------|
| TBA-PW12/CeO2 | 689  | 1.3        | 14.9       | 20.6      | 43.4      | 6.4        | 260            | 83.3          |
| Ce2(WO4)3/CeO2 | 649  | 0.9        | 13.6       | 18.5      | 39.0      | 5.3        | 225            | 73.9          |
| WO3/CeO2 | 634  | 0.8        | 14.3       | 20.8      | 32.4      | 4.6        | 145            | 74.0          |
| Ce2(WO4)3 | 659  | 0.7        | 9.7        | 11.6      | 41.2      | 4.0        | 189            | 53.3          |
| WO3 | 484  | 0.2        | 0.0        | 2.5       | 0.0       | 0.0        | 54             | 0.2           |

### Table 2. Effect of reaction field on catalytic activity over Ce2(WO4)3/CeO2 with and without an electric field. *Feed gas, CH4:O2:Ar = 25:15:60 SCCM; input current, 3.0 mA; catalyst weight, 100 mg; furnace temperature, 423 K. *Feed gas, CH4:O2:Ar = 25:15:60 SCCM; catalyst weight, 100 mg; furnace temperature, 573–1073 K. *Catalyst bed temperature measured using a thermocouple.

| Conditions | External temp./K | CH4 Conv./% | O2 Conv./% | C2 Sel./% | C2 Yield/% |
|-----------|-----------------|-------------|-----------|-----------|-----------|
| with EF (3.0 mA) | 423 (649) | 13.6 | 18.5 | 39.0 | 5.3 |
| without EF | 573 | 0.0 | 0.5 | 0.0 | 0.0 |
| 673 | 0.0 | 0.7 | 0.0 | 0.0 |
| 773 | 0.0 | 1.6 | 0.0 | 0.0 |
| 873 | 0.1 | 2.5 | 0.0 | 0.0 |
| 973 | 0.5 | 2.1 | 0.0 | 0.0 |
| 1073 | 6.0 | 14.8 | 2.1 | 0.1 |
Next, to clarify the reaction mechanism, the influence of contact time (W/F CH₄) on OCM activity over Ce₂(WO₄)₃/CeO₂ in the electric field was investigated. As presented in Fig. 2, CH₄ conversion and O₂ conversion increased and C₂ selectivity decreased concomitantly with increasing contact time. The decrease of C₂ selectivity resulted from combustion of C₂ hydrocarbons with O₂ in gas phase.

Figure 3 shows the relation between CH₄ conversion and C₂H₄, C₂H₆, and C₂H₂ selectivity over Ce₂(WO₄)₃/CeO₂ in the electric field (423 K, 3.0 mA). As shown in Fig. 3, as CH₄ conversion approaches 0%, C₂H₄ and C₂H₆ selectivity increase and C₂H₂ selectivity decreases. In the range of very low CH₄ conversion, production of C₂H₄ and C₂H₆ were the main reactions. One can infer that methyl radical and carbene were produced on the catalyst surface in the electric field. Accordingly, Ce₂(WO₄)₃ can extract one or two H atoms from CH₄ and produced methyl radical and carbene. However, C₂H₂ selectivity increased concomitantly with increased CH₄ conversion up to 15% and then decreased. These results suggest that C₂H₂ was generated through oxidative dehydrogenation of C₂H₄ or through coupling of CH species, which was formed from CH₄ with electric energy³³; then it was oxidized to CO and CO₂.

To confirm that reactive oxygen species are formed on the catalyst surface in the electric field, the periodic operation test at 473 K over Ce₂(WO₄)₃/CeO₂ catalyst was conducted with the electric field. Results of activity tests are presented in Table 4. The results were the activities at 2 min after from methane + Ar supply. Table 4 shows that the C₂ selectivity was higher than 60% and that it was maintained during three cycles. When increasing the CH₄ conversion by increasing the contact time, C₂ selectivity was higher than 65% and was maintained during three cycles. However, in the periodic operation test without an electric field at 1073 K, C₂ selectivity was very low; CO and CO₂ were mainly formed (Supplementary Information Table S7). These results demonstrate that reactive oxygen species suitable for OCM were formed on the catalyst surface in the electric field. The synergic effect of Ce₂(WO₄)₃ and electric field created the reactive oxygen species for selective oxidation of methane and activated methane because the active site structure for OCM with the electric field was Ce₂(WO₄)₃.

**In-situ Raman over Ce₂(WO₄)₃/CeO₂ with and without electric field.** Many researchers have reported that Na₂WO₄-Mn₂O₃/SiO₂ catalyst has high OCM activity²,³⁴. A short W–O bond in the distorted WO₄ unit is proposed as the active site of Na₂WO₄-Mn₂O₃/SiO₂. This W–O bond is observed at 927 cm⁻¹ in Raman spectrum³⁵. Specific examination of the Ce₂(WO₄)₃ structure reveals that it has WO₄ units of two kinds. Both are physically distorted. It is likely that W–O bonds in Ce₂(WO₄)₃/CeO₂ work as an active site for OCM in the electric field. Comparison of Ce₂(WO₄)₃ with Na₂WO₄ reveals that Ce₂(WO₄)₃ has a stable structure and short W–O bonds in the distorted WO₄ unit, which are observed at 949 cm⁻¹ and 931 cm⁻¹³². We conducted in-situ Raman measurements over Ce₂(WO₄)₃/CeO₂ in the electric field to clarify the W–O bond behavior in the electric field. Figure 4 portrays Raman spectra with and without the electric field.

| Furnace temp./K | Tc/K | Voltage/kV | CH₄ Conv./% | O₂ Conv./% | C₂ Sel./% | C₂ Yield/% | Field intensity/V mm⁻¹ |
|----------------|------|------------|-------------|------------|-----------|------------|------------------------|
| 423            | 649  | 0.9        | 13.6        | 18.5       | 39.0      | 5.3        | 225                    |
| 673            | 793  | 0.6        | 7.5         | 25.5       | 38.4      | 2.9        | 146                    |
| 873            | 931  | 0.3        | 4.7         | 31.5       | 21.4      | 1.0        | 71                     |

Table 3. Temperature dependency over Ce₂(WO₄)₃/CeO₂ in the electric field. *Feed gas, CH₄/O₂/Ar = 25:15:60 SCCM; input current, 3.0 mA; catalyst weight, 100 mg; furnace temperature, 423, 673, 873 K. *Catalyst bed temperature measured using a thermocouple.
in distorted WO₄ unit are summarized in Supplementary Information Table S8. Figure 4 shows that the spectra of Ce₂(WO₄)₃/CeO₂ with an electric field (Fig. 4c–e) differed from inert (Fig. 4a) and the peak of W–O bonds shifted to a lower wavenumber and broadened. From Supplementary Information Table S8, the peak shift of W–O peaks in the electric field was about 7–10 cm⁻¹. The shift and broadening of the W–O peaks were attributed to the electric field because the spectrum without electric field after imposing electric field in CH₄+O₂ flow (Fig. 4f) was almost identical to that of the spectrum without an electric field under inert (Fig. 4a). These results suggest that the Ce₂(WO₄)₃/CeO₂ structure was distorted and that the W–O bonds were weakened by the electric field. It acted as the reactive oxygen suitable for selective oxidation of methane to C₂ hydrocarbons. For comparison, the Raman spectrum over Ce₂(WO₄)₃/CeO₂ at 603–703 K without an electric field (Fig. 4b) was measured because the catalyst bed temperature was increased by Joule heating in the electric field. The shift of W–O peaks was about 2–3 cm⁻¹, indicating a small effect of Joule heat from the electric field on W–O bond activation. These results imply that W–O bond activation is attributable mainly to the electric field and that the W–O bond activated by the electric field functioned as an active site for OCM in the electric field.

Next, XAFS spectra were recorded. The results are presented in Supplementary Information Figs S7 and S8 and Table S9. Regarding the coordination number of W–O bonds in Ce₂(WO₄)₃ from XAFS measurements, the catalyst after 1 cycle in periodic operation test in the electric field showed a smaller coordination number than in the as-made material and after O₂ supply in the periodic operation test in the electric field. This result supports our inference that surface oxygen of Ce₂(WO₄)₃ activated by the electric field was consumed by methane. Therefore, results of XAFS, in-situ Raman, and periodic operation tests demonstrated that OCM which occurred as lattice oxygen in Ce₂(WO₄)₃ (short W–O bonds in distorted WO₄ unit) was consumed and reproduced by the redox mechanism. A possible reaction mechanism is described in Supplementary Information Fig. S9. In addition, redox reaction of Ce cation (Ce³⁺ ↔ Ce⁴⁺ + e⁻) might be also responsible for the OCM reaction.
Conclusion

Oxidative coupling of methane (OCM) over 40 wt% TBA-PW₁₂O₄₀/CeO₂ in the electric field was conducted. The catalyst showed high OCM activity, although the catalyst showed extremely low OCM activity, even at the high temperature of 1073 K without an electric field. After reaction with the electric field, Raman spectra confirmed that the structure of TBA-PW₁₂O₄₀/CeO₂ catalyst was changed to Ce₂(WO₄)₃/CeO₂.

Then, OCM activities over Ce₂(WO₄)₃/CeO₂, WO₃/CeO₂, Ce₂(WO₄)₃, and WO₃ catalysts in an electric field (3.0 mA) were investigated to clarify the structure of the active site. Ce₂(WO₄)₃/CeO₂, WO₃/CeO₂, and Ce₂(WO₄)₃ catalysts showed OCM activity; WO₃ showed no OCM activity. After reaction with the electric field, Raman spectra showed that W species in WO₃/CeO₂ changed to Ce₂(WO₄)₃ from WO₃. Therefore, the active site structure for OCM with the electric field was Ce₂(WO₄)₃.

Figure 4. Raman spectra of Ce₂(WO₄)₃/CeO₂ with and without electric field: (a) inert at room temperature, (b) without EF in air at 603–703 K, (c) 6.0 mA in air (0.69 kV), (d) 6.0 mA in CH₄ (0.73 kV), (e) 6.0 mA in CH₄ + O₂ (0.67 kV), and (f) without EF after (e).
Also, Ce2(WO4)3/CeO2 catalyst showed extremely low OCM activity at 1073 K. In the periodic operation test over Ce2(WO4)3/CeO2 catalyst, C2 selectivity was higher than 60% and was maintained during three cycles. Therefore, synergetic effects of Ce2(WO4)3 and the electric field created the reactive oxygen species suitable for selective oxidation of methane, activated methane, and progressed OCM only when an electric field was applied.

Results of XAFS, in-situ Raman and periodic operation test demonstrated that OCM occurred using the lattice oxygen of Ce2(WO4)3 (short W–O bonds in distorted WO4 unit), which were consumed and reproduced by the redox mechanism in the electric field.

Methods

Catalyst preparation. Tetraethylammonium (TBA) salt of Keggin-type HPAs (denoted as TBA-HPAs), such as (TBA)₃₉[PW₁₂.V₂O₄₀] (x = 0, 1, 2; n = 3, 4, 5), were prepared according to the published procedure with some modifications. They were analyzed using IR spectroscopy (see Supplementary Information). As a reference catalyst, WO₃ (Kanto Chemical Co. Inc.) was used as supplied. All other chemicals were reagent-grade; they were used as supplied.

Keggin-type TBA-HPAs supported on CeO₂ (JRC-CEO-1) catalysts were prepared by impregnation with acetone as the impregnation solvent. The loading amount of TBA-HPAs was 40 wt%. First, acetone (30 mL) and CeO₂ (0.6 g) were added to a 300 mL glass beaker and were stirred for 2 h using a mechanical stirrer. Subsequently, TBA-HPAs (0.4 g) dissolved into acetone (10 mL) were added dropwise into the flask and were stirred for 2 h again. The resulting suspension was dried. Then the resulting solid was dried overnight at 393 K.

WO₃/CeO₂ catalyst containing 11.9 wt% W was prepared using impregnation with water as the impregnation solvent, as described in a previous report. An ammonium metatungstate hydrate ((NH₄)₆H₂W₁₂O₄₀·H₂O) was used as a precursor. After impregnation, the resulting suspension was dried. Then the resulting solid was dried at 393 K overnight, followed by calcination for 3 h in air at 773 K under a ramping rate of 0.5 K min⁻¹.

Ce₂(WO₄)₃/CeO₂ catalyst containing 11.9 wt% W was prepared by impregnating CeO₂ with an aqueous solution of ammonium metatungstate hydrate using a similar method to that for WO₃/CeO₂, except that the calcination temperature was 1173 K. As a reference, unsupported Ce₂(WO₄)₃ was prepared using a complex method combining ethylenediamine tetraacetic acid and citrate ions, as described in previous reports. The catalyst was sieved into 355–500 μm. A schematic image of the reaction system is presented in Supplementary Information Fig. S10. The catalyst was sieved into 355–500 μm. Then 100 mg of it was charged in the reactor. The reactant feed gases were methane, oxygen, and Ar (CH₄: O₂: Ar = 25: 15: 60, total flow rate: 100 SCCM). The effect of contact time (W/FCH₄) was investigated by changing the total flow rate. The standard W/FCH₄ was 1.6 gcat h⁻₁ mol⁻¹. For the reaction in the electric field, two stainless steel electrodes (2.0 mm o.d.) were inserted contiguously into the catalyst bed in the reactor. The electric field was controlled using a constant current (3, 5, or 7 mA) with a DC power supply. The imposed voltage depended on the electric properties of the catalyst. Current and voltage profiles were measured using an oscilloscope (TDS 3052B; Tektronix Inc.). The reactor temperature was set to 423 K to avoid the condensation of water produced by the reactions, except for reactions that used no electric field. Product gases were analyzed at 5 min after oxygen supply, and at 2 and 12 min after methane supply (COₓ and Ar supply) with a GC-TCD (GC-2014; Shimadzu Corp.) with a molecular sieve 5A packed column. The respective calculation formulae for conversion, C₂ yield, C₂ selectivity, and Faradaic number in this study are shown below (eqs 2–6).

CH₄ Conversion (%) = \( \frac{\text{Carbon moles of } (\text{CO}, \text{CO}_2, \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \text{and } \text{C}_2\text{H}_2)}{\text{Carbon moles of input methane}} \times 100 \) (2)

O₂ Conversion (%) = \( \frac{\text{Consumption moles of O}_2}{\text{Input oxygen moles}} \times 100 \) (3)

C₂ Yield, C₂−based = \( \frac{\text{Carbon moles of } (\text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \text{and } \text{C}_2\text{H}_2)}{\text{Carbon moles of input methane}} \times 100 \) (4)

C₂ Selectivity, C₂−based = \( \frac{\text{C₂ Yield}}{\text{CH₄ Conversion}} \times 100 \) (5)

Faradaic number = \( \frac{\text{Carbon moles of reacted methane}}{\text{Moles of input electron}} \) (6)

A periodic operation test was conducted to elucidate surface active species on the catalyst in the following steps. In the first step, oxygen and Ar were supplied to the reactor with an electric field for 10 min for oxidation of the catalyst surface. For the second step, residual oxygen in the gas phase of the reactor was removed with Ar purge for 5 min. For the third step, methane and Ar were supplied to the reactor with an electric field for 12 min to evaluate the oxidation catalysis of the surface oxygen species on the catalyst. As the final step, Ar purge was conducted for 20 min to remove all residual gases. The steps described above were repeated for three cycles. Product gases were analyzed at 5 min after oxygen + Ar supply, and at 2 and 12 min after methane + Ar supply (COₓ and desorbed CH₄) were detected at 5 min after from oxygen + Ar supply and no products were detected at 12 min after
from methane + Ar supply). Gas flow was O₂: Ar = 1:10, total 55 mL min⁻¹ (for oxidation of the catalyst surface) and CH₄: Ar = 1: 10 or 1:2, total 55 or 75 mL min⁻¹ (for oxidation of supplied methane by surface oxygen species). The reactor temperature was fixed at 473 K. The imposed current was set at 3.0 or 7.0 mA.

Characterization of catalyst. FT-IR spectra were recorded on a spectrometer (FT-IR-6200; Jasco Corp.) using a KBr pelleting method. Raman spectra were recorded on a Raman spectrometer (excitation line X = 532 nm, NRS-1000; Jasco Corp.). The crystalline structure was characterized using powder X-ray diffraction (XRD, RINT-Ultima III; Rigaku Corp.) operating at 40 kV and 40 mA with Cu-Kα radiation. The specific surface area of the catalyst was measured using N₂ adsorption using the BET method (Gemini VII; Micromeritics Instrument Corp.) after pre-treatment at 473 K in N₂ atmosphere for 2 h. Results of BET measurements are presented in Supplementary Information Table S10. W L₃-edge X-ray absorption fine structure (XAFS) spectra were recorded on BL14B2 in SPring-8 (Hyogo, Japan). Catalysts treated in the reaction condition were ground into powder and were pressed into pellets. Then, pellets were packed into gas-barrier bags. The pellets were diluted with BN to adjust for XAFS measurement. EXAFS analysis and curve fitting were performed using software (Athena ver. 0.8.056; Artemis ver. 0.8.012).

In-situ Raman. In-situ Raman measurements in the electric field were conducted using a Raman spectrometer with a hand-made glass reactor and gold wire electrodes (see Supplementary Information Fig. S11). The reactant feed gases were supplied with canned standard gases (CH₄(0.995%) + Ar and/or O₂(99.9%)). The electric field was imposed using a constant current at 6.0 mA.

Raman spectra for catalyst heated at reaction temperature (603–703 K) without an electric field were also observed to elucidate the effect of Joule heating on the catalyst structure. A Ni-Cr wire was inserted into the sample for heating by resistance heating.

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Author Contributions
K.S. and S.O. designed the experiments, analyzed data, and wrote the manuscript. K.S. and K.I. conducted experimental work. T.Y. assisted in analyses of results. Y.S. supervised the project and revised the manuscript text. All authors participated in discussion of the research and review of the manuscript.

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