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Ambient-temperature Oxidative Coupling of Methane in an Electric Field by a Cerium Phosphate Nanorod Catalyst

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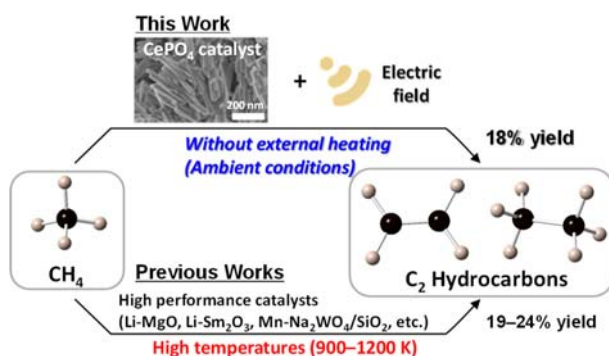
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A CePO₄ nanorod with the uniform surface Ce sites could work as a durable catalyst and showed the highest C₂ yield of 18% in the electric field without the need for external heating, which was comparable to those for the reported high performance catalysts at high temperature (>900 K).

Methane, a principle component of natural gas, has attracted much attention because it is abundant and distributed worldwide.¹ However, methane is mostly combusted for heating and little are used for hydrogen production by steam reforming;^{1, 2} thus, methane is an underutilized resource to produce chemical products. Since oxidative coupling of methane (OCM) is a useful reaction to directly convert methane to high value-added C₂ hydrocarbons,^{1–6} various non-catalytic and catalytic processes have been developed for OCM reactions from the 1980s.^{2–10} However, most systems typically require high reaction temperatures over 900 K for OCM reaction,^{3–6} leading to low selectivity to C₂ hydrocarbons due to an overoxidation of the more reactive C₂ hydrocarbon products than methane.^{3–6} Despite extensive studies on the developments of highly active and selective OCM catalysts over 40 years, the C₂ hydrocarbon yields have been limited so far to less than 25%, the majority was below 20%, in the high temperature range (900–1200 K).^{4–6, 10–14} Therefore, the development of novel catalytic systems to efficiently promote the selective OCM reaction even in low temperature region remains a challenging subject of research.

We have very recently reported that the application of electric field to Ce-W-O catalyst systems enables the selective OCM reaction even at low temperatures such as 423 K^{15–17} and

proposed the formation of active oxygen species involving the redox reaction of a Ce cation.¹⁸ However, these systems (e.g., Ce₂(WO₄)₃/CeO₂) have several drawbacks; (i) the need for a CeO₂ support leads to difficult structure control of surface active Ce sites, (ii) and low surface areas (~4 m²/g), and (iii) which results in insufficient C₂ yield (~6%). Herein, we focus on the OCM activity of a monoclinic CePO₄ nanorod catalyst with structurally controlled uniform active sites.¹⁹ The present system has significant advantages of high C₂ yields (18%) and durability in sharp contrast to other cerium-based catalysts. This study provides the first example of the catalytic application of CePO₄ to OCM at low-temperature in the electric field (Scheme 1).



Scheme 1. Low-temperature OCM by a monoclinic CePO₄ nanorod catalyst combined with an electric field.

Monoclinic CePO₄ synthesized using a hydrothermal method could act as an efficient acid-base bifunctional solid catalyst for chemoselective acetalization.¹⁹ Although the IR measurements for a sample with adsorbed probe molecules (pyridine, chloroform, acetone, and methanol) indicated the presence of uniform Lewis acid and weak base sites, the detailed surface structure of CePO₄ was still unclear. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and

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fast Fourier transform (FFT) pattern are shown in Figures 1(a) and S1. The HAADF-STEM results proved that the dominant facets exposed on CePO_4 nanorods are (110) and (100), especially (110) is more dominant (see the details in the Figure S1). The amount of surface Ce cations at (110) and (100) facets are estimated to be 1.6 and 2.2 nm^{-2} , respectively (Figures 1(b) and 1(c)), in good agreement with the experimental one (1.6 nm^{-2}) calculated from the BET surface area of CePO_4 (37 $\text{m}^2 \text{g}^{-1}$) and the surface Ce cations with Lewis acid sites measured using pyridine-IR (96 $\mu\text{mol g}^{-1}$)¹⁹ (see the details in the Electronic Supplementary Information). These results support the presence of uniform surface Ce species on CePO_4 nanorods.

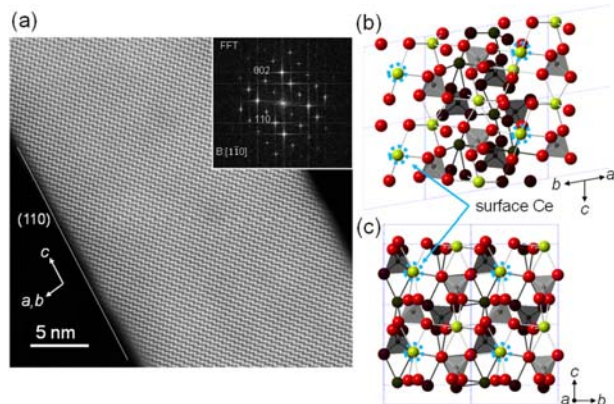


Figure 1. (a) The TEM image with FFT pattern and (b) the (110) surface and (c) the (100) surface structure of monoclinic CePO_4 catalyst.

Then, activity tests for OCM in the electric field (7 mA) over various cerium-based catalysts including CePO_4 were conducted without external heating. Figure 2 shows the time course of the C_2 hydrocarbon yield for OCM over various Ce-based catalysts (CePO_4 , $\text{Ce}_2(\text{WO}_4)_3$, $\text{Ce}_2(\text{MoO}_4)_3$, CeVO_4 , and CeO_2) and the details are shown in Table S1. XRD patterns and BET surface area of the catalysts are shown in Figure S2. The full details about the characterization of CePO_4 including IR spectroscopy for a sample with adsorbed probe molecules, SEM image and XPS (Ce species in CePO_4 was Ce^{3+}) have been already reported in the previous paper.¹⁹ Among the catalysts tested, CePO_4 catalyst showed the highest C_2 hydrocarbon yield (about 18%) in the electric field without external heating. The OCM activity of CePO_4 catalyst at low temperature (542 K) with the electric field is comparable to that of $\text{Mn-Na}_2\text{WO}_4/\text{support}$ system catalysts at 1073 K¹¹ which is one of the highest performance catalysts. Although the catalytic activity of CePO_4 did not change for 1 h, the C_2 hydrocarbon yields rapidly decreased in the case of $\text{Ce}_2(\text{WO}_4)_3$ and $\text{Ce}_2(\text{MoO}_4)_3$. In addition, CeVO_4 , and CeO_2 were almost ineffective; thus, the CePO_4 catalyst exhibited high and stable OCM activity in the electric field. There was no significant difference in the XRD patterns between the fresh and spent CePO_4 (Figure S3), which indicates the high durability of monoclinic CePO_4 during the reaction even in the electric field. As shown in Table S2, the catalyst-bed temperature increased to 542 K in the electric field (7 mA) because of Joule heat and reaction heat. However, the CePO_4 catalyst showed low OCM

activity without the electric field even at high temperature of 1073 K. Therefore, the effect of Joule heat by the imposed electric field was not important in this low-temperature catalytic system, and the CePO_4 catalyst can activate methane only when the electric field is applied.

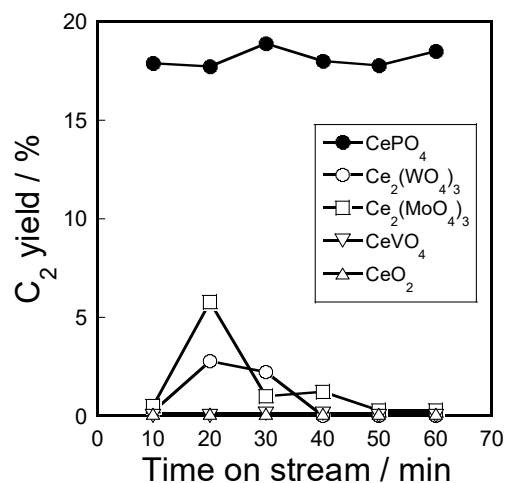


Figure 2. Time course of the C_2 hydrocarbon yield for OCM over various cerium-based catalysts at ambient temperature in the electric field: $\text{CH}_4:\text{O}_2:\text{Ar} = 15:12:33$, total flow rate 60 SCCM; catalyst, 100 mg; current, 7.0 mA; furnace temperature, without external heating (299 K).

To investigate the reaction mechanism, periodic operation tests over the CePO_4 catalyst with the electric field were conducted; First, the catalyst was pretreated with O_2 in the electric field, and then the methane was introduced in the electric field (see the details in the Electronic Supplementary Information). Figure S4 shows time course of the formation rate of C_2 hydrocarbons during methane supply in the periodic operation test with the electric field. The C_2 hydrocarbons formation gradually decreased and almost completed within 5 min. After the catalyst was regenerated by the O_2 treatment in the electric field, the C_2 formation rate was almost the same as that of the first cycle. In addition, there was no significant difference in the catalytic activity and C_2 selectivity (>75%) for the periodic operation tests (5 cycles) with the electric field as shown in Figure 3. In contrast, for the periodic operation test without the electric field, C_2 selectivity (<20%) and the CH_4 conversion (<1%) were very low even at high temperature of 1073 K as presented in Figure S5. These results indicated that the active oxygen species was formed on the catalyst surface by the reaction with O_2 in the electric field and such species were consumed by the reaction with methane in the electric field.²⁰

The amounts of active oxygen species for productions of C_2 and CO_x were determined from the integrated product yields in the periodic operation tests during methane supply after O_2 pre-treatment in the electric field (Figures 4 and S6). The consumed active oxygen species for C_2 production was estimated to be 93 $\mu\text{mol-O}_2 \text{g-cat}^{-1}$ during methane supply, and the value was almost equal to the number of surface Ce site on the CePO_4 catalyst (96 $\mu\text{mol g-cat}^{-1}$) as mentioned above.¹⁹ The Raman measurements were conducted for the recovered CePO_4

catalysts after both O₂ treatment and reaction with CH₄ in the electric field to evaluate active oxygen species on the surface Ce sites of CePO₄.²¹ As shown in Figure S7, the Raman band at 538 cm⁻¹ appeared after the O₂ treatment in the electric field while it completely disappeared after the reaction with CH₄ in the electric field. It has been reported that the Ce–O bands of active oxygen species on CeO₂ are observed in the range of 340–540 cm⁻¹.^{22–24} Therefore, the 538 cm⁻¹-band would be related to active oxygen species on CePO₄. The potentials of Ce–O species for the activation of small hydrocarbons including CH₄ have been proposed;^{25–27} thus, such species suitable for C₂ production is possibly formed on the CePO₄ catalyst through the activation of O₂ molecule on the surface Ce sites assisted by the electric field, which results in OCM reaction even at low temperature.

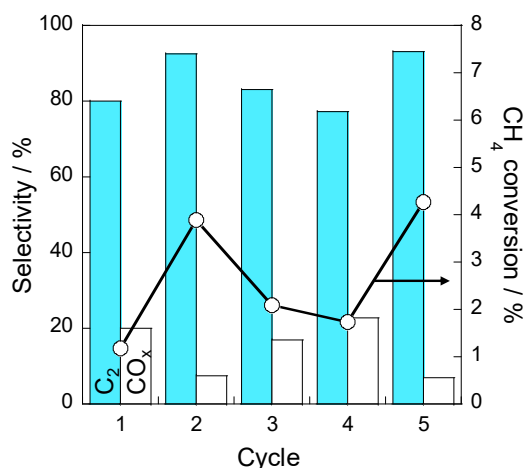


Figure 3. Results of periodic operation tests after 2 min of methane supply over CePO₄ catalyst with the electric field at 473 K: (light blue bar) C₂ selectivity; (white bar) CO_x selectivity; (○) CH₄ conversion.

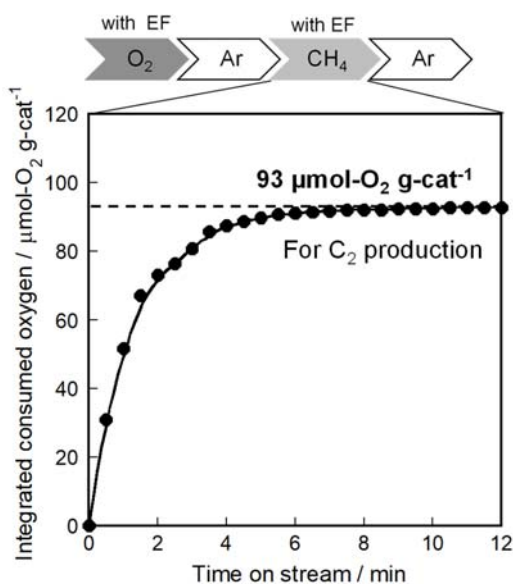


Figure 4. Integrated consumed active oxygen species during methane supply over CePO₄ catalyst in the electric field after O₂ pre-treatment in the electric field.

In conclusion, CePO₄ catalyst with the uniform surface Ce species showed the high activity and stability for low-temperature oxidative coupling of methane (C₂ yield = 18%) in the electric field without external heating. In the electric field, formation and regeneration of the surface active oxygen species over the surface Ce sites of CePO₄ proceeded easily even at low-temperature, and thereby OCM proceeds effectively through consumption and reproduction of the active oxygen species. The present study provide design for high performance catalysts: The Ce-based catalyst with high specific surface area and uniform active sites will show a high OCM activity. The combination of uniform active sites and electric field can be an effective approach to avoid undesirable reactions thanks to the lowering reaction temperature and will open the door for highly selective catalytic oxidation reaction under mild conditions.

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Conflicts of interest

There are no conflicts to declare.

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