

# Effects of electric field on fine structure and activity of $\text{Ln}_2(\text{WO}_4)_3$ catalysts for oxidative coupling of methane at low temperature

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**Abstract:** Effects of electric field on fine structure and activity of  $\text{Ln}_2(\text{WO}_4)_3$  catalysts for low temperature oxidative coupling of methane (OCM) were investigated. Activity tests revealed that  $\text{Ln}_2(\text{WO}_4)_3$  catalysts with the redox active Ln cations (Ce, Pr, Sm, Eu, and Tb) showed OCM activity. First-principles calculations indicated that  $\text{Ce}^{3+}$  species in  $\text{Ce}_2(\text{WO}_4)_3$  structure were oxidized to  $\text{Ce}^{4+}$  species in the electric field by extracting electrons from the Ce 4f orbitals near the Fermi level, thereby its structure was distorted. The redox reaction of Ce cations and structure distortion in  $\text{Ce}_2(\text{WO}_4)_3$  seem to contribute to high OCM activity in the electric field.

**Keywords:** Oxidative coupling of methane, Electric field,  $\text{Ce}_2(\text{WO}_4)_3$ .

## 1. Introduction

Oxidative coupling of methane (OCM) is one of effective means of utilizing natural gas: useful  $\text{C}_2$  hydrocarbons are produced directly from methane using air as an oxidizing agent. Because of its stable tetrahedral structure, activation of methane requires high temperatures over 973 K and non-selective oxidation proceeds at such high temperatures. To resolve the difficulties described above, we adopted a non-conventional catalytic system, a catalytic reaction in an electric field, in anticipation of methane conversion at low temperatures. Recent reports have described that OCM proceeds selectively even at a low temperatures (423 K) in an electric field over Ce–W–O system catalysts with a  $\text{Ce}_2(\text{WO}_4)_3$  structure.<sup>1-3</sup> In the present work, the reaction mechanism of OCM over  $\text{Ce}_2(\text{WO}_4)_3$  catalyst in the electric field were investigated. The influence of Ce cations in the  $\text{Ce}_2(\text{WO}_4)_3$  catalyst was evaluated by comparing the OCM activity over various  $\text{Ln}_2(\text{WO}_4)_3$  (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, and Dy) catalysts in the electric field. The relation between the distorted  $\text{Ce}_2(\text{WO}_4)_3$  structure and methane activation was examined using first-principles calculation.

## 2. Experimental

$\text{Ce}_2(\text{WO}_4)_3$  catalyst was prepared using a complex polymerization method combining ethylenediamine tetraacetic acid and citrate ions, as described in an earlier report.<sup>4</sup> The other  $\text{Ln}_2(\text{WO}_4)_3$  (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, and Dy) catalysts were prepared as described in a previous report,<sup>5</sup> with some modifications.

Catalytic activity tests were conducted with a fixed bed flow type reactor equipped with a quartz tube (4.0 mm i.d.). The catalyst was sieved into 355-500  $\mu\text{m}$  and 100 mg of it was charged in the reactor. Reactant feed gases were methane, oxygen and Ar ( $\text{CH}_4 : \text{O}_2 : \text{Ar} = 25 : 15 : 60$ , total flow rate: 100 SCCM). For the reaction in the electric field, two stainless steel electrodes (2.0 mm o.d.) were inserted contiguously to the catalyst bed in the reactor. The electric field was imposed using a constant current with a DC power supply. The temperature of reactor was set at 423 K to avoid the condensation of water produced by the reactions. Product gases after passing a cold trap were analyzed using a GC-FID with a methanizer (Ru/ $\text{Al}_2\text{O}_3$  catalyst), and a GC-TCD.

All calculations were conducted with the Vienna *ab-initio* simulation package (VASP ver. 5.3.3). Core electrons were represented with the projector-augmented wave (PAW) method. PBE exchange-correlation functional was used for spin-polarized DFT calculation. GGA+U approach was adopted to describe highly localized electrons such as *f* electrons. We applied  $U_{\text{eff}}$  as  $U$  on the Ce 4*f* electrons ( $U_{\text{eff}} = 3.5$  eV). Cut off energy was 500 eV. The effect of electric field was considered by removing electrons from the unit cell.

### 3. Results and discussion

To elucidate the role of Ce in  $\text{Ce}_2(\text{WO}_4)_3$  catalyst on the OCM activity, catalytic oxidative coupling of methane over various  $\text{Ln}_2(\text{WO}_4)_3$  ( $\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, and Dy}$ ) catalysts was conducted with an electric field at 423 K (Figure 1). Results revealed that  $\text{Ln}_2(\text{WO}_4)_3$  catalysts with redox active Ln cations (Ce, Pr, Sm, Eu, and Tb) showed OCM activity in the electric field even at low temperature (423 K).

Then, to confirm the correlation between the OCM activity and the lattice strain and/or the redox reaction of Ln cations, theoretical investigations were conducted. First-principles calculations indicated that the Ce 4*f* orbital near the Fermi level works as a donor orbital. Therefore, electric field effects were evaluated by removing electrons from this donor orbital. When electrons were removed from the unit cell of  $\text{Ce}_2(\text{WO}_4)_3$ , electrons were extracted from the Ce 4*f* orbitals. These results showed that some parts of  $\text{Ce}^{3+}$  species in  $\text{Ce}_2(\text{WO}_4)_3$  structure were oxidized to  $\text{Ce}^{4+}$  species in the electric field by extracting electrons from the Ce 4*f* orbitals near the Fermi level.

Next, we investigated the structural change of  $\text{Ce}_2(\text{WO}_4)_3$  when electrons were extracted from the system by imposing the electric field. All Ce–O bond lengths decreased and some W–O bond lengths increased concomitantly with increasing the number of removed electrons (increasing positive charge). The changes in bond lengths were attributable to the decrease in the ion radius of Ce cations, which resulted from the oxidation of Ce cations from  $\text{Ce}^{3+}$  to  $\text{Ce}^{4+}$  in the electric field (positively charged). *In-situ* Raman measurements also showed that W–O bonds in  $\text{Ce}_2(\text{WO}_4)_3$  were weakened (*i.e.* increase in W–O bond length) by the electric field.<sup>1</sup> The distorted lattice oxygen seems to act as an active oxygen species suitable for the OCM reaction. These results showed that the redox reaction of Ln cations in  $\text{Ln}_2(\text{WO}_4)_3$  induced by the electric field brought the lattice strain and high OCM activity in the electric field.

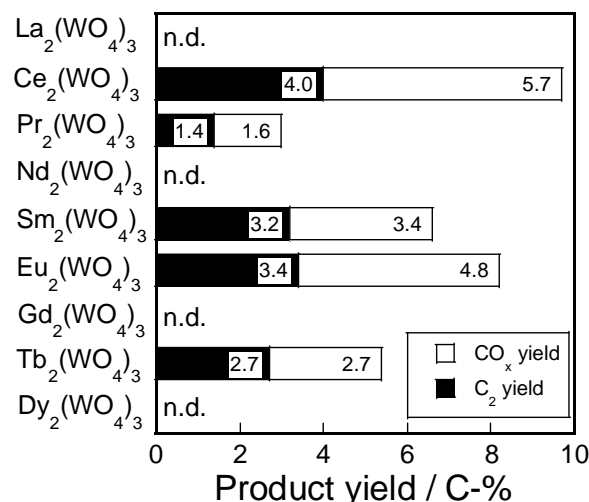


Figure 1. OCM over  $\text{Ln}_2(\text{WO}_4)_3$  catalysts in the electric field.

### 4. Conclusions

$\text{Ln}_2(\text{WO}_4)_3$  catalysts with redox active Ln cations (Ce, Pr, Sm, Eu, and Tb) showed OCM activities. First-principles calculations indicated that  $\text{Ce}^{3+}$  species in  $\text{Ce}_2(\text{WO}_4)_3$  structure were oxidized to  $\text{Ce}^{4+}$  species in the electric field by extracting electrons from the Ce 4*f* orbitals near the Fermi level, thereby its structure was distorted. The redox reaction of Ln cations in  $\text{Ln}_2(\text{WO}_4)_3$  induced by the electric field brought the lattice strain and high OCM activity in the electric field.

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