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Catalytic oxidative conversion of methane and ethane over polyoxometalate-derived catalysts in electric field at low temperature

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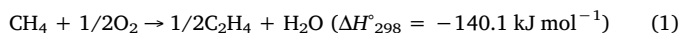
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ABSTRACT

We examined oxidative coupling of methane (OCM) and oxidative dehydrogenation of ethane (ODE) over various polyoxometalate supported CeO₂ catalysts at 423 K in an electric field. Tetrabutylammonium (TBA) salt of Keggin-type phosphotungstate (PW₁₂O₄₀) supported CeO₂ catalysts ((TBA)₃PW₁₂O₄₀/CeO₂) showed high activities for OCM and ODE in the electric field (3 mA) at 423 K, although the catalyst without the electric field showed extremely low activities at such low temperature. FT-IR spectra and XRD patterns confirmed that the structure of (TBA)₃PW₁₂O₄₀/CeO₂ was changed to Ce₂(WO₄)₃/CeO₂ after reactions with the electric field, and it acted as an active site structure for OCM and ODE with the electric field. Results of activity tests revealed that the C₂H₆ production was a main reaction in OCM with the electric field, and C₂H₄ was formed through a successive oxidative dehydrogenation of the formed C₂H₆. Periodic operation tests demonstrated that reactive oxygen species suitable for ODE were formed on the catalyst surface of Ce₂(WO₄)₃ in the electric field.

1. Introduction

Natural gas is being discovered in many countries around the world. The United States has extracted large amounts of shale gas. Nevertheless, the state of natural gas, especially methane, is gaseous at room temperature and atmospheric pressures. Therefore, it is transported using gas pipelines or LNG systems. Small to 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. We specifically focused on direct catalytic methane conversion to C₂ hydrocarbons by oxidative coupling of methane (OCM) [1–10]. The formula can be described as presented below (Eq. (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,

anticipating methane activation at low temperatures. Results show that various low-temperature catalytic reactions such as methane steam reforming [11–17] 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) catalyst [14,17–19] and Ce-W-O system catalysts [17,20]. Especially, Ce-W-O system catalysts with a Ce₂(WO₄)₃ structure, which derived from Keggin-type polyoxometalates (POMs) supported CeO₂, showed the high CH₄ conversion and C₂ selectivity in the electric field at 423 K.

In this study, we specifically examined various polyoxometalate supported catalysts for catalytic oxidative conversions of methane and ethane in the electric field at low temperature. The effects of catalyst composition, imposed current, contact time, and other parameters on the catalytic activity and selectivity were investigated. An active structure was characterized using powder X-ray diffraction and FT-IR spectroscopy.

2. Experimental

2.1. Catalyst preparation

Tetrabutylammonium (TBA) and Cesium salts of Keggin-type polyoxometalates (POMs), such as (TBA)₃PM₁₂O₄₀ and Cs₃PM₁₂O₄₀ (M = Mo, W) (denoted as TBA-POMs and Cs-POMs), were prepared

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according to the published procedure with some modifications [20–24]. They were analyzed using FT-IR spectroscopy (see Supporting Information). $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (denoted as H-POMs) were used as supplied (Wako Pure Chemical Industry Ltd.). All other chemicals were reagent-grade; they were used as supplied.

Keggin-type TBA-POMs supported on CeO_2 (JRC-CEO-1) catalysts were prepared by impregnation method with acetone as the impregnation solvent [20]. The loading amount of TBA-POMs was 40 wt%. First, acetone (30 mL) and CeO_2 (0.6 g) were added to a 300 mL eggplant flask and were stirred for 2 h using a rotary evaporator. Subsequently, TBA-POMs (0.4 g) dissolved into acetone (10 mL) were added to the flask and were stirred for 2 h again. The resulting suspension was dried up on a hot plate while stirring. Then the resulting solid was dried overnight at 393 K.

Keggin-type Cs-POMs or H-POMs supported on CeO_2 catalysts were prepared using a similar method to that for TBA-POMs/ CeO_2 , except that the impregnation solvent was water.

As a reference catalyst, $\text{Ce}_2(\text{WO}_4)_3/\text{CeO}_2$ catalyst containing 11.9 wt% W was prepared using an impregnation method with water as the impregnation solvent, as described in previous reports [20,25]. An ammonium metatungstate hydrate ($(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}\cdot\text{H}_2\text{O}$) was used as a precursor. After impregnation, the resulting suspension was dried up on a hot plate while stirring. Then the resulting solid was dried at 393 K overnight, followed by calcination for 3 h in air at 1173 K under a ramping rate of 0.5 K min^{-1} .

2.2. Activity test

2.2.1. Catalytic oxidative coupling of methane

Catalytic oxidative coupling of methane was conducted with a fixed bed flow-type reactor equipped with a quartz tube (4.0 mm i.d.). A schematic image of the reaction system is presented in Supporting Information Fig. S1. 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 ($\text{CH}_4:\text{O}_2:\text{Ar} = 25:15:60$, total flow rate 100 SCCM). The effect of contact time (W/F_{CH_4}) was investigated by changing the total flow rate. The standard W/F_{CH_4} was $1.5 \text{ g}_{\text{cat}} \text{ h mol}^{-1}$. 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. And a thermocouple was inserted into the catalyst-bed to measure the reaction temperature. 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 2001C; 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 after passing a cold trap were analyzed using a GC-FID (GC-14B; Shimadzu Corp.) with a Porapak N packed column and methanizer (Ru/ Al_2O_3 catalyst), and using a GC-TCD (GC-2014; Shimadzu Corp.) with a molecular sieve 5A packed column. In gaseous products, CO, CO_2 , C_2H_6 , C_2H_4 , and C_2H_2 were detected however C_{3+} hydrocarbons were not detected. The respective calculation formulae for conversion, C_2 yield, and C_2 selectivity in this study are shown below (Eqs. (2)–(5)).

$$\text{CH}_4\text{Conversion}(\%) = \frac{\text{Carbonmolesof}(\text{CO}, \text{CO}_2, \text{C}_2\text{H}_6, \text{C}_2\text{H}_4, \text{and} \text{C}_2\text{H}_2)}{\text{Carbonmolesofinputmethane}} \times 100 \quad (2)$$

$$\text{O}_2\text{Conversion}(\%) = \frac{\text{ConsumptionmolesofO}_2}{\text{Inputoxygenmoles}} \times 100 \quad (3)$$

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

$$\text{C}_2\text{Selectivity}(\%, \text{C-based}) = \frac{\text{C}_2\text{Yield}}{\text{CH}_4\text{Conversion}} \times 100 \quad (5)$$

2.2.2. Catalytic dehydrogenation of ethane

Catalytic conversions of ethane with or without the electric field in the presence of oxygen were conducted using the reactor as described above. The catalyst was sieved into 355–500 μm and 100–200 mg of it was charged in the reactor. The reactant feed gases were ethane, oxygen, and argon ($\text{C}_2\text{H}_6:\text{O}_2:\text{Ar} = 25:15:60$, total flow rate 100 SCCM). The $W/F_{\text{C}_2\text{H}_6}$ was $1.5\text{--}3.0 \text{ g}_{\text{cat}} \text{ h mol}^{-1}$. 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 after passing a cold trap were analyzed using the GC-FID and the GC-TCD. In gaseous products, CO, CO_2 , CH_4 , C_2H_4 , and C_2H_2 were detected however C_{3+} hydrocarbons were not detected. The calculation formula for C_2H_6 conversion in this study is shown below (Eq. (6)).

$$\text{C}_2\text{H}_6\text{Conversion}(\%) = \frac{\text{Carbonmolesof}(\text{CO}, \text{CO}_2, \text{CH}_4, \text{C}_2\text{H}_4, \text{and} \text{C}_2\text{H}_2)}{\text{Carbonmolesofinputethane}} \times 100 \quad (6)$$

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, ethane 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 four cycles. Product gases were analyzed at 5 min after oxygen + Ar supply, and at 2 min after ethane + Ar supply (CO_x and desorbed C_2H_6 were detected at 5 min after from oxygen + Ar supply). Gas flow was $\text{O}_2:\text{Ar} = 5:50$, total flow rate 55 SCCM (for oxidation of the catalyst surface) and $\text{C}_2\text{H}_6:\text{Ar} = 5:50$, total flow rate 55 SCCM (for oxidation of supplied ethane by surface oxygen species). The reactor temperature was fixed at 473 K. The imposed current was set at 3.0 mA.

2.3. Characterization

FT-IR spectra were recorded on a spectrometer (FT-IR/6200; Jasco Corp.) using a KBr pelletizing method. The crystalline structure was characterized using powder X-ray diffraction (XRD, RINT-Ultima III; Rigaku Corp.) operating at 40 kV and 40 mA with $\text{Cu-K}\alpha$ radiation.

3. Results and discussion

3.1. Oxidative coupling of methane over POMs/ CeO_2 in an electric field

First, catalytic oxidative coupling of methane (OCM) over various polyoxometalates (POMs) supported CeO_2 catalysts in the electric field were conducted at furnace temperature of 423 K. Table 1 shows the results of the activity tests. Table S1 shows the temperature increase and the reaction enthalpy with the imposed electric power. CH_4 conversion and C_2 yield were in following order: TBA-PW $_{12}\text{O}_{40}/\text{CeO}_2 > \text{Cs-PW}_{12}\text{O}_{40}/\text{CeO}_2 > \text{TBA-PMO}_{12}\text{O}_{40}/\text{CeO}_2 > \text{Cs-PMO}_{12}\text{O}_{40}/\text{CeO}_2 > \text{H-PW}_{12}\text{O}_{40}/\text{CeO}_2 > \text{H-PMO}_{12}\text{O}_{40}/\text{CeO}_2$. PW $_{12}\text{O}_{40}/\text{CeO}_2$ series showed higher activity and C_2 selectivity than those of PMO $_{12}\text{O}_{40}/\text{CeO}_2$ series. Counter cation of POMs also affected on the activity and the selectivity. Among the tested POMs/ CeO_2 catalysts, TBA-PW $_{12}\text{O}_{40}/\text{CeO}_2$ catalyst showed the highest CH_4 conversion (14.9%) and C_2 yield (6.5%) in the electric field (3.0 mA) at furnace temperature of 423 K. However, as shown in Fig. S2, the counter cations of PW $_{12}\text{O}_{40}/\text{CeO}_2$ had the small impact on C_2 hydrocarbon selectivity. Similar to our previous report [20], the OCM activity

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