

Low-temperature oxidative coupling of methane over various cerium-based catalysts in the electric field

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Abstract: Oxidative coupling of methane (OCM) with the electric field over various cerium-based catalysts was investigated at low temperature (423 K). Among the tested catalysts, CePO₄ catalyst had high OCM activity at the low temperature range with the electric field. On the other hand, the catalyst showed low OCM activity even in the high temperature range without the electric field. Since the C₂ selectivity decreased as the furnace temperature increased, the effect of the Joule heating by the electric field is unimportant in the system. The electric field contributed to high OCM activity of CePO₄ catalyst at low temperature.

Keywords: Oxidative coupling of methane, Electric field, Cerium-based catalysts.

1. Introduction

Oxidative coupling of methane (OCM) is a direct conversion of methane to valuable C₂ hydrocarbons. However, OCM reaction requires high temperatures over 973 K since methane has a stable structure. At such high temperature, non-selective oxidation will proceed and the C₂ yield will drastically decrease. To solve this problem, a new process for converting methane to ethane and ethylene is required. We adopted a non-conventional system, a catalytic reaction in an electric field, to activate methane at low temperature such as 423 K. In the previous study, we found that Ce-W-O system catalysts had high OCM activity in the electric field. The redox reaction of Ce cations introduced by the electric field might bring the lattice strain and high OCM activity.¹⁻³ Therefore, it is considered that other cerium-based catalysts might also have OCM activity at low temperatures with the electric field. In this research, we investigated Ce(MO_x)_y system catalysts for OCM reaction at low temperatures in the electric field.

2. Experimental

CePO₄ catalyst was synthesized by a hydrothermal method using Ce(NO₃)₃•6H₂O and (NH₄)₂HPO₄ as precursors.⁴ Hydrothermal synthesis was conducted using a stainless steel autoclave with a Teflon vessel liner at 453 K for 96 h. The obtained solid was calcined at 1173 K for 3 h.

Catalytic activity tests were conducted with a fix-bed flow type reactor. The catalyst (100 mg) was charged in the reactor and two stainless steel electrodes were inserted contiguously to the catalyst-bed. Reactant feed gas was methane, oxygen and argon (CH₄:O₂:Ar = 25:15:60 total gas flow 100 SCCM). The electric field was imposed using a constant current from 3.0 to 7.0 mA. To compare the activity tests without the electric field were also conducted at the temperature range from 573 K to 1073 K. Furnace temperature was set to 423 K to avoid condensation of water produced by the reaction. Product gas was analyzed using GC-FID and GC-TCD.

3. Results and discussion

The catalytic activity tests over various cerium-based catalysts were conducted in the electric field at 423 K. Among the catalysts, CePO₄ catalyst showed the highest OCM activity in the electric field. Figures 1 and 2 show the relationship between catalyst-bed temperature and CH₄ conversion or C₂ selectivity with and without the electric field. CePO₄ catalyst showed high OCM activity in the electric field (CH₄ conversion

61.1%, C₂ selectivity 30.2% at input current 7.0 mA). However, without the electric field, CePO₄ catalyst showed no OCM activity in such low temperature range. Also, the catalyst without the electric field showed low OCM activity even at 1073 K.

In the OCM reaction with the electric field, the catalyst-bed temperature increased by Joule heat. To elucidate the influence of Joule heat in the OCM reaction in the electric field, the furnace temperature was changed from 423 K to 673 K and 873 K. As the furnace temperature raised, the C₂ selectivity decreased which was probably caused by the combustion of C₂ products. Therefore, the effect of Joule heating by the electric field is unimportant in the system.

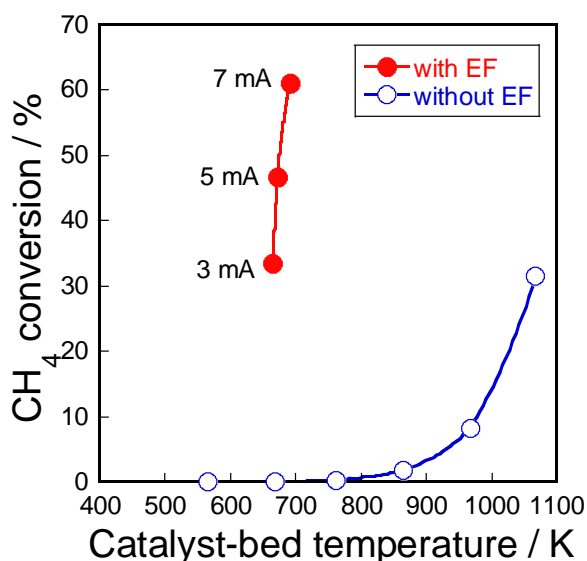


Figure 1. CH₄ conversion over CePO₄ catalyst with or without electric field.

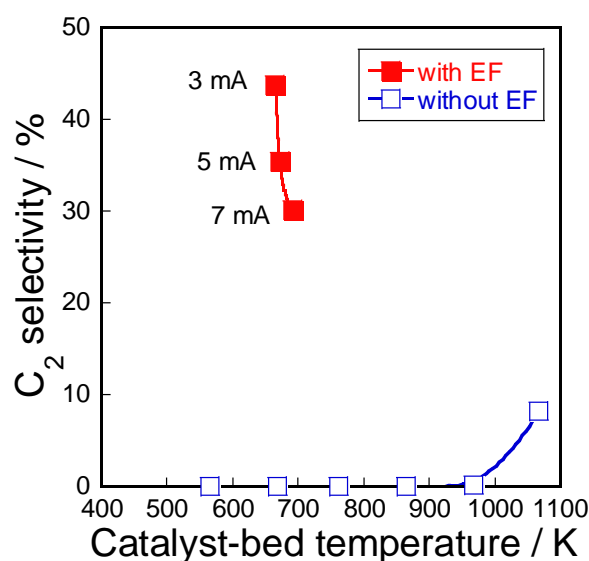


Figure 2. C₂ selectivity over CePO₄ catalyst with or without electric field.

4. Conclusions

CePO₄ catalyst had high OCM activity in the electric field at low temperature such as 423 K, although the CePO₄ catalyst showed extremely low OCM activity without the electric field even at high temperature such as 1073 K. Also, this high OCM activity was not related to the Joule heat from the electric field. The electric field contributed to the high OCM activity over CePO₄ catalyst at low temperatures.

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