

# Low-Temperature Catalytic Oxidative Coupling of Methane over Supported Heteropolytungstate Catalysts in an Electric Field

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Direct conversion of methane to ethane and ethylene by oxidative coupling of methane (OCM) is anticipated as a highly efficient reaction. Although OCM has been investigated actively, activation of methane requires high temperatures over 973 K and non-selective oxidation proceeds at such high temperatures. To solve these problems, we adopted a non-conventional system, a catalytic reaction in an electric field, in anticipation of activation of methane at low temperatures [1]. We have reported that OCM proceeded at low temperatures (423 K) in an electric field over Ce-W-O system catalysts, including Keggin-type heteropolytungstate [1,2]. Here we report the mechanism of C<sub>2</sub> hydrocarbon formation during OCM in the electric field over supported heteropolytungstate catalysts.

Tetrabutylammonium (TBA) salt of heteropolytungstate, TBA<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] (denoted as TBA-PW<sub>12</sub>O<sub>40</sub>), supported on CeO<sub>2</sub> (JRC-CEO-1) catalysts were prepared by an impregnation method [1]. Loading amount of TBA-PW<sub>12</sub>O<sub>40</sub> was 40wt%.

The catalytic activity tests were conducted with a fixed-bed flow-type quartz tube reactor. A 100 mg of catalyst was charged in the reactor. Reactant feed gases were methane (or ethane), oxygen and Ar (CH<sub>4</sub>:O<sub>2</sub>:Ar = 25:15:60, total flow rate: 100-180 SCCM). For the reaction in the electric field, two stainless steel electrodes 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 423 K to avoid the condensation of water produced by the reactions. Products were analyzed using a GC-FID with a methanizer and a GC-TCD.

Figure 1 shows a relation between CH<sub>4</sub> conversion and selectivity over the TBA-

PW<sub>12</sub>O<sub>40</sub>/CeO<sub>2</sub> catalyst in the electric field. As CH<sub>4</sub> conversion approaches 0 %, C<sub>2</sub>H<sub>6</sub> selectivity increases, and each selectivity of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> decreases. In the range of very low CH<sub>4</sub> conversions, C<sub>2</sub>H<sub>6</sub> production was the main reaction in the OCM with the electric field. C<sub>2</sub>H<sub>4</sub> selectivity increased concomitantly with increased CH<sub>4</sub> conversion and C<sub>2</sub>H<sub>6</sub> selectivity decreased. These results revealed that the C<sub>2</sub>H<sub>6</sub> production was a main reaction in OCM with the electric field, and C<sub>2</sub>H<sub>4</sub> was formed through a successive oxidative dehydrogenation of the formed C<sub>2</sub>H<sub>6</sub>.

To evaluate the reaction mechanism of C<sub>2</sub> hydrocarbon formation during OCM in the electric field, catalytic conversion of ethane over TBA-PW<sub>12</sub>O<sub>40</sub>/CeO<sub>2</sub> catalyst was conducted in the electric field at 423 K. As shown in Table 1, TBA-PW<sub>12</sub>O<sub>40</sub>/CeO<sub>2</sub> catalyst showed high C<sub>2</sub>H<sub>4</sub> selectivity and maintained its structure even at high C<sub>2</sub>H<sub>6</sub> conversion. These results indicated that the oxidative dehydrogenation of C<sub>2</sub>H<sub>6</sub> to C<sub>2</sub>H<sub>4</sub> easily proceeds, however, a successive dehydrogenation of C<sub>2</sub>H<sub>4</sub> to C<sub>2</sub>H<sub>2</sub> is unfavorable reaction over the catalyst in the electric field.

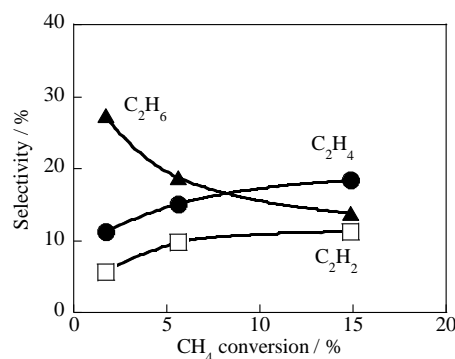


Fig. 1 Relation between CH<sub>4</sub> conversion and C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> selectivity over TBA-PW<sub>12</sub>O<sub>40</sub>/CeO<sub>2</sub> catalyst in the electric field (423 K, 3 mA).

Table 1 Oxidative dehydrogenation of ethane over TBA-PW<sub>12</sub>O<sub>40</sub>/CeO<sub>2</sub> catalyst in the electric field

Current / mA	Voltage / V	Conv. / %		Selectivity / C-%				
		C <sub>2</sub> H <sub>6</sub>	O <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	CH <sub>4</sub>	CO	CO <sub>2</sub>
3.0	700	2.2	9.4	63.9	0.0	3.7	21.0	11.4
5.0	600	3.7	9.4	74.3	0.0	6.0	13.0	6.7
7.0	400	8.5	13.4	73.3	0.9	7.2	12.2	6.4

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## REFERENCES

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- [2] K. Sugiura, S. Ogo, K. Iwasaki, T. Yabe, Y. Sekine, *Scientific Reports*, 6 (2016) 25154.