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# High Catalytic Activity of $Sm_2O_3$ for Oxidative Coupling of Methane into Ethane and Ethylene

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The catalytic activity of $Sm_2O_3$ for oxidative coupling of $CH_4$ was measured at the conditions: $P(CH_4)/P(O_2)=6$, $P(O_2)=14.5$ kPa, $W/F=0.000223-0.0891$ $g \cdot h \cdot l^{-1}$, and $T=750$ °C. STY of $C_2$-compounds reached to 2.98 $mol \cdot g^{-1} \cdot h^{-1}$ at W/F of 0.000223 $g \cdot h \cdot l^{-1}$. The catalytic activity of $Sm_2O_3$ was one to three orders of magnitude greater than those reported for other metal oxides.

Oxidative coupling of $CH_4$ into $C_2H_6$ and $C_2H_4$ ($C_2$-compounds) attracted much attention since the pioneering work done by Keller and Bhasin.[1-7] We have reported that $Sm_2O_3$ is an active and selective catalyst for this reaction.[8a,c] However, low pressure of oxygen (0.4 kPa), high $P(CH_4):P(O_2)$ ratio (45), and slow flow rate of reactant (4.5 $ml \cdot min^{-1}$) applied for the test of the catalyst were not suitable for evaluating the true catalytic activity of $Sm_2O_3$ because the conversion of oxygen exceeded 95%. In this communication, we will describe the catalytic activity of $Sm_2O_3$ measured under higher $P(O_2)$, lower $P(CH_4):P(O_2)$, and larger flow rate than the conditions used previously.[8a,c,d]

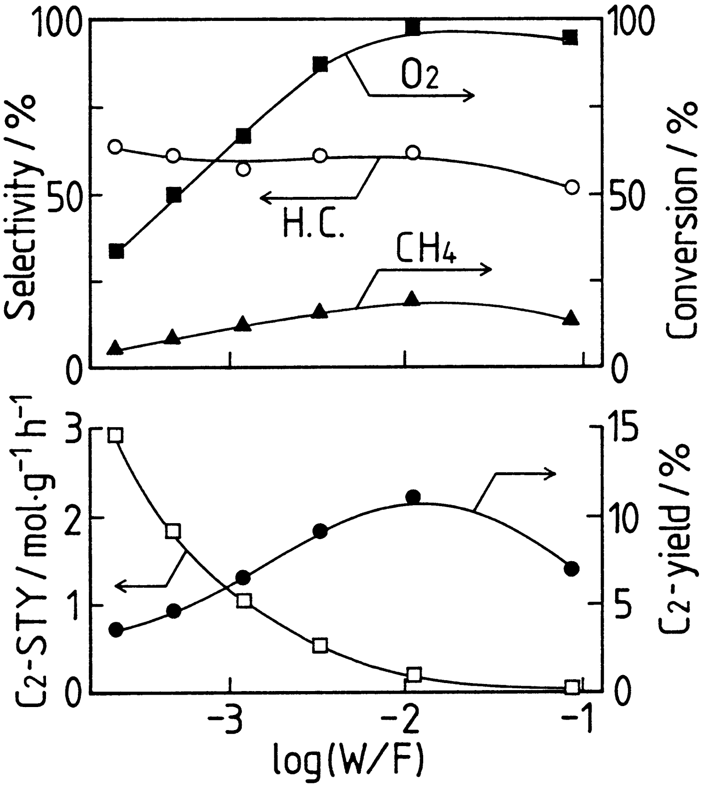

Fig. 1. The effect of W/F.

The $Sm_2O_3$ powder (purity>99.9%) used was obtained from Asahi Chemical Industry Co. The experiments were carried out using a fixed-bed reactor with a conventional gas-flow system at a total pressure of 101 kPa. The conversion of methane, the selectivities of the products were calculated on the basis of carbon number of $CH_4$ reacted.

Figure 1 shows the effect of W/F (weight of $Sm_2O_3$/flow rate of reactant, 0.000223-0.0891 $g\cdot h\cdot l^{-1}$ (W=0.010-0.150 g, F=1.68-45.0 $l\cdot h^{-1}$)) on $C_2$-STY (space time yield of $C_2$-compounds), $C_2$-yield, selectivity to higher hydrocarbons ($=C_2+C_3+C_4$, $C_2/C_2+C_3+C_4>0.85$), $CH_4$-conversion, and $O_2$-conversion. The experiments were carried out at 750 °C and $P(CH_4):P(O_2)=6:1$. The $O_2$-conversion was greater than 95% when W/F was larger than 0.01 $g\cdot h\cdot l^{-1}$. At lower W/F than this value, $O_2$-conversion decreased with a decrease in W/F. $C_2$-STY increased remarkably as decreasing W/F. $C_2$-STY reached to 2.98 $mol\cdot g^{-1}\cdot h^{-1}$ at 0.000223 $g\cdot h\cdot l^{-1}$ of W/F. The selectivity to the coupling products (mainly $C_2$-hydrocarbons) at this W/F was fairly high (64%).

The $C_2$-STY reported previously for different catalysts are shown in Table 1. Since the experimental conditions used for testing the catalytic activities are so different each other in Table 1, we cannot compare true catalytic activities of the catalysts. However, the $C_2$-STY observed for $Sm_2O_3$ in this work were one to three orders of magnitude greater than the values reported previously.[1-7,9]

High stability,[8c] high $C_2$-selectivity, and high catalytic activity observed for $Sm_2O_3$ suggest that this oxide is one of the most promising catalysts for practical use in converting natural gas into $C_2$-hydrocarbons.

Table 1. Comparison of the activities of catalysts for oxidative coupling of $CH_4$

| Catalyst | $C_2$-STY $mmol\cdot g^{-1}\cdot h^{-1}$ | $C_2$-select. % | Temp °C | $P(CH_4)$ kPa | $P(CH_4)/P(O_2)$ | W/F $g\cdot h\cdot l^{-1}$ | Ref.No. |
|---|---|---|---|---|---|---|---|
| $PbO/SiO_2$ | 1.2 | 71.4 | 740 | 70 | 10 | 0.43 | 2 |
| Li/MgO | 0.9 | 46.5 | 720 | 29 | 1.9 | 1.3 | 3 |
| PbO/MgO | 11.1 | 85.3 | 750 | 61 | 37.8 | 0.045 | 6 |
| $LaAlO_3$ | 62.3 | 78 | 710 | 88 | 33.3 | 0.017 | 4 |
| Li/Mn-oxide | 13.5 | 43 | 750 | 57 | 2.0 | 0.167 | 8b |
| $K/BaCO_3$ | 0.21 | 42 | 800 | 2.8 | 2.0 | 22.2 | 5 |
| Li/ZnO | 3.31 | 61 | 740 | 55 | 2.1 | 0.67 | 7 |
| $K/Bi/Al_2O_3$ | 90 | 30 | 700 | 51 | 10 | 0.0029 | 9 |
| $Sm_2O_3$ | 527 | 61 | 750 | 87 | 6.0 | 0.0033 | This work |
| $Sm_2O_3$ | 2980 | 60 | 750 | 87 | 6.0 | 0.000223 | This work |

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