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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·h·l^{-1}, and T=750 °C. STY of C_2-compounds reached to 2.98 mol·g^{-1}·h^{-1} at W/F of 0.000223 g·h·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·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]

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

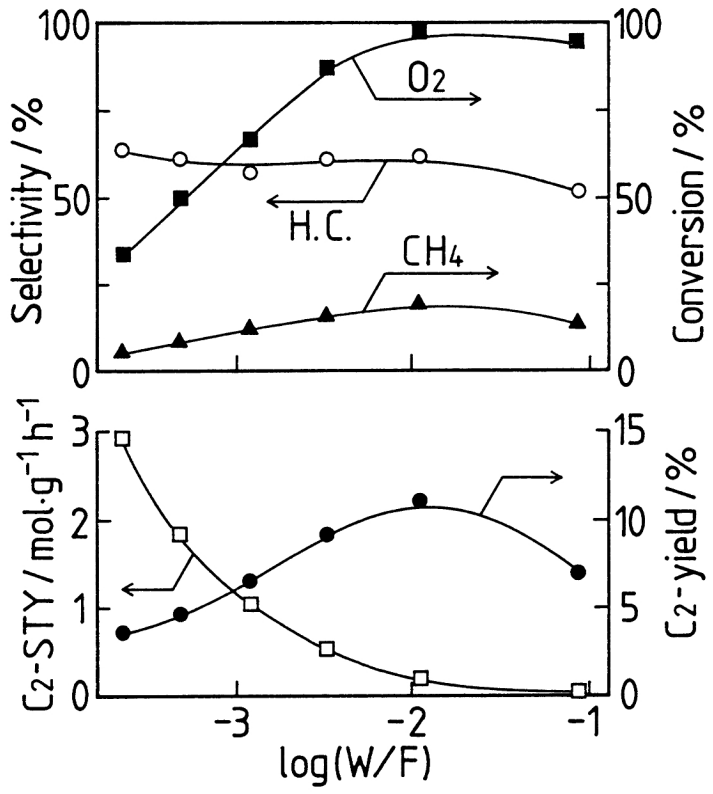

Fig. 1. The effect of W/F.

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	C_2-select.	Temp	$P(CH_4)$	$P(CH_4)/P(O_2)$	W/F	Ref.No.
	$mmol \cdot g^{-1} \cdot h^{-1}$	%	°C	kPa		$g \cdot h \cdot l^{-1}$	
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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