

Selective Synthesis of Ethylene by Partial Oxidation of Methane over LiCl-Sm₂O₃

Kiyoshi Otsuka,* Qin Liu, and Akira Morikawa

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

Methane is partially oxidised over LiCl-Sm₂O₃ catalyst to give C₂-compounds (ethylene and ethane) in 7.2—19.9% C₂-yield at 750 °C, with a high C₂H₄:C₂H₆ ratio.

Although the catalytic partial oxidation of methane is of potential technological importance, there have been only a few fundamental reports on this reaction.^{1—4} We have already reported that samarium oxide is an active and selective catalyst in the oxidative coupling of methane.⁴ An Sm₂O₃

catalyst containing added alkali metal carbonate showed better catalytic activity and selectivity giving a C₂-yield of 21%.⁵ It is believed that oxidative coupling of methane is initiated by the abstraction of H from CH₄ to form CH₃ radicals,³ and that C₂H₆ is produced by a coupling between

Table 1. Effects of lithium salts on the results of partial oxidation of CH₄.^a

Catalyst	% CH ₄ - conversion	% C ₂ H ₄ - selectivity	% C ₂ H ₆ - selectivity	% C ₂ - yield	% C ₂ H ₄ - yield
Sm ₂ O ₃	30.2	22.8	18.4	12.4	6.9
LiBr-Sm ₂ O ₃	30.4	25.4	12.8	11.6	7.7
LiCl-Sm ₂ O ₃	28.8	58.2	10.8	19.9	16.8
LiF-Sm ₂ O ₃	26.5	26.3	26.3	13.9	7.0
LiOH-Sm ₂ O ₃	38.2	26.7	24.4	19.5	10.2
LiNO ₃ -Sm ₂ O ₃	37.5	28.0	23.9	19.5	10.5
Li ₂ CO ₃ -Sm ₂ O ₃	41.2	26.4	27.7	22.3	10.9

^a Reaction conditions: $T = 750\text{ }^{\circ}\text{C}$, $p(\text{CH}_4) = 0.05\text{ atm}$, $p(\text{CH}_4)/p(\text{O}_2) = 5/2$, catalyst weight/flow rate = $600\text{ g l}^{-1}\text{ s}$.

Table 2. Effect of the pressure of reactants on the results of partial oxidation of CH₄.^a

Pressure of reactants /atm	% CH ₄ - conversion	% C ₂ H ₄ - selectivity	% C ₂ H ₆ - selectivity	% C ₂ - yield	% C ₂ H ₄ - yield
0.07	24.6	50.5	12.9	15.6	12.4
0.14	31.1	41.7	8.0	15.5	13.0
0.28	40.2	31.4	4.1	14.3	12.6
0.42	44.4	25.0	3.6	12.7	11.1
0.56	34.6	20.2	4.8	8.7	7.0
0.70	30.3	22.3	5.0	8.3	6.8
0.84	26.9	20.6	6.3	7.2	5.5
0.98	33.3	18.0	4.7	7.6	6.0

^a Reaction conditions: $T = 750\text{ }^{\circ}\text{C}$, $p(\text{CH}_4)/p(\text{O}_2) = 5/2$, catalyst weight/flow rate = $2400\text{ g l}^{-1}\text{ s}$.

two CH₃ radicals. The subsequent oxidative dehydrogenation of C₂H₆ produces C₂H₄.^{2,3,5} Usually the C₂-compounds produced from methane oxidation consist of C₂H₆ in preference to C₂H₄ as C₂H₆ is oxidized preferentially to CO and CO₂, and a low selectivity of C₂H₄ is observed under the reaction conditions in which methane can be activated. Thus the subsequent conversion of C₂H₆ into C₂H₄ is usually necessary. Therefore, catalysts which convert CH₄ directly into C₂H₄ with high selectivity are desirable. We report here the selective synthesis of ethylene from methane over LiCl-Sm₂O₃ catalyst.

Powder catalysts of alkali metal salts-Sm₂O₃, containing 20 mol% alkali metal, were prepared from lithium salts and Sm₂O₃. The experiments were carried out using a conventional gas-flow system at atmospheric pressure.

Table 1 shows the effects of adding different lithium salts to Sm₂O₃ on the conversion of methane, the selectivities of C₂H₄ and C₂H₆, and the C₂-yield (C₂H₄+C₂H₆). The selectivities of C₂H₄ and C₂H₆ were defined as the yields of C₂H₄ and C₂H₆, respectively, as a percentage of the CH₄ conversion. The Sm₂O₃ catalysts prepared with LiOH, LiNO₃, and Li₂CO₃ increased both the conversion and the C₂-selectivities, resulting in a considerable increase in C₂-yield (19.5–22.2%) compared with Sm₂O₃ alone. The addition of LiCl did not increase the conversion of methane, but enhanced specifically the selectivity of C₂H₄.

Table 2 shows the effect of total pressure of CH₄ and O₂ on the reaction. The ratio of C₂H₄:C₂H₆ was 7.7–3.3 for pressures of 0.07–0.98 atm. The yield of C₂H₄ at a pressure of reactants less than 0.30 atm was 12.4–13.0%. The yield of C₂H₄ for LiCl-Sm₂O₃ shown in Table 1 was 16.8%. These yields are considerably better than results reported in the literature for other metal oxide catalysts.^{1–3}

Thus, LiCl-Sm₂O₃ may be a useful catalyst in the selective synthesis of C₂H₄ from CH₄. The favourable effect observed on addition of LiCl to Sm₂O₃ is due to depression of the further oxidation of CH₄ and C₂H₆ to CO and CO₂.

Received, 2nd January 1986; Com. 003

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