Active Catalysts in Oxidative Coupling of Methane

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The NaCl/Mn-oxide catalyst shows higher catalytic activity than any previously reported in converting methane into ethylene and higher alkenes with yields of 15.7—30.6% at 750 °C.

Oxidative dehydrogenation and coupling of CH_4 producing C_2 hydrocarbons (C_2H_6 + C_2H_4) has attracted much attention since the pioneering work of Keller and Bhasin.[1] Many groups[2—7] are working in this area and there is increasing industrial activity.[8] However, the reactivities of the catalysts reported recently for synthesizing C_2 hydrocarbons are still not satisfactory.

We have already reported that the oxides of the first-row transition elements, such as the oxides of Ni, Ti, and Zn, containing lithium chloride had high catalytic activities in the selective synthesis of C_2H_4 from CH_4.[4c] The highest space time yields (S.T.Y.) observed for the synthesis of C_2 hydrocarbons were 27 and 11 mmol (g-cat)$^{-1}$ h^{-1} for the LiCl-added manganese oxide (denoted as LiCl/Mn-oxide) and LiCl/Ni-oxide, respectively.

Tentative experiments showed that the addition of NaCl instead of LiCl to manganese oxides gave better C_2-S.T.Y. (S.T.Y. for the synthesis of C_2 hydrocarbons) compared to that for LiCl/Mn-oxide. However, NaCl/Ni-oxide did not show better catalytic activity in the synthesis of C_2 compounds than that observed for LiCl/Ni-oxide. We now report results for NaCl/Mn-oxides which show better catalytic activities than literature values.[1—7]

Powdered NaCl/Mn-oxides catalysts, containing 20 mol% sodium metal, were prepared from NaCl and MnO_2 as the initial manganese oxide. The catalysts were pretreated in air at 750 °C for 2 h before use. The catalysts were studied using a fixed-bed reactor with a conventional gas-flow system at atmospheric pressure using helium as carrier gas. The products after 25 min on stream were measured by gas chromatography. The conversion of CH_4, the selectivities, and the yields of the products were calculated on the basis of carbon number of CH_4 reacted.

Table 1 shows the conversions of CH_4 and O_2, the selectivity for hydrocarbon formation ($\geqslant C_2$), and the yields of hydrocarbons observed for NaCl/Mn-oxide and LiCl/Ni-oxide catalysts. The former catalyst was mechanically mixed with quartz sand (5 g) as a diluent before being packed in the reactor because the dispersion of the catalyst increased the total yields of hydrocarbons. The experimental conditions are given in Table 1. Oxygen-containing organic compounds such as MeOH and HCHO were not produced. As can be seen in Table 1, the main products are C_2H_4 under any conditions tested. It is to be noted that C_3H_6, C_4H_8, benzene, and toluene are also produced. The selectivity for the formation of total hydrocarbons ($\geqslant C_2$) observed for NaCl/Mn-oxide at a pressure of reactant 0.09 atm reached 30.6%. S.T.Y.s of C_2 compounds (C_2H_4 + C_2H_6) and of total hydrocarbons ($\geqslant C_2$) increased linearly with increasing pressure of reactants. The highest S.T.Y.s of total hydrocarbons observed are 72.3 mmol (g-cat)$^{-1}$ h^{-1} (48.2 mmol m^{-2} h^{-1}) for NaCl/Mn-oxide and 18.5 mmol (g-cat)$^{-1}$ h^{-1} (43.0 mmol m^{-2} h^{-1}) for LiCl/Ni-oxide. The highest C_2-S.T.Y. in Table 1 is 64.0 mmol (g-cat)$^{-1}$ h^{-1} (42.7 mmol m^{-2} h^{-1}) for NaCl/Mn-oxide. These values are higher than any previously reported.[1—7] For example, the highest C_2-S.T.Y. previously observed for LiCl/Mn-oxide was 27 mmol (g-cat)$^{-1}$ h^{-1} under the conditions T = 750 °C, $P(CH_4) + P(O_2) = 0.84$ atm, $P(CH_4) : P(O_2) = 2 : 1$, total gas flow rate = 100 ml min^{-1}, weight of catalyst = 1.00 g.[4c] The C_2-S.T.Y. observed for NaCl/Mn-oxide in Table 1 under similar conditions is 50.4 mmol (g-cat)$^{-1}$ h^{-1}, 1.9 times greater than the value for the LiCl/Mn-oxide. Since the oxygen in the reactants was almost completely consumed (O_2 conversion >93%) during passage through the catalyst bed, we can expect higher S.T.Y.s than those in Table 1 when the flow rate of the reactants and the partial pressure of oxygen are increased further than the conditions described in Table 1.

The NaCl/Mn-oxide is superior to the LiCl/Mn-oxide for the

Table 1. Pressure effects on the yields and S.T.Y.s of the products in partial oxidation of methane over NaCl/Mn-oxide and LiCl/Ni-oxide.[a]

Catalyst	NaCl/Mn-oxide						LiCl/Ni-oxide
$P(CH_4) + P(O_2)$/atm	0.09	0.19	0.34	0.64	0.83	1.00	0.83
Catalyst weight/g	0.40	0.40	0.40	0.40	0.40	0.25	1.00
CH_4 conversion/%	46.8	46.1	41.5	38.9	36.1	32.0	31.9
O_2 conversion/%	99.4	98.8	99.5	92.9	97.4	97.6	93.5
% Selectivity to hydrocarbons ($\geqslant C_2$)	65.2	56.0	51.4	45.5	53.1	48.9	49.0
% Yields							
C_2H_4	25.7	19.8	16.8	14.2	14.9	11.9	11.3
C_2H_6	1.7	2.2	2.6	1.9	2.2	2.0	3.2
C_3H_6	0.5	0.6	0.7	0.9	1.1	0.9	0.5
C_4H_8	1.9	2.8	0.9	0.4	0.7	0.5	0.5
Benzene + toluene	0.8	0.4	0.4	0.2	0.3	0.2	0.1
Total hydrocarbons	30.6	25.8	21.3	17.6	19.2	15.7	15.7
S.T.Y./mmol (g-cat)$^{-1}$ h^{-1}							
$C_2H_4 + C_2H_6$	9.2	14.7	23.4	36.7	50.4	64.0	17.2
Total hydrocarbons	10.2	17.3	25.7	40.1	56.6	72.3	18.5

[a] Reaction conditions: T = 750 °C; $P(CH_4) : P(O_2) = 2 : 1$, total gas flow rate = 100 ml min^{-1}.

following reasons. (i) As described above, the catalytic activity of the NaCl/Mn-oxide is greater than that of the LiCl/Mn-oxide. (ii) Deactivation of the latter catalyst commenced after 2 h stream, but no deactivation of the former catalyst was observed after 8 h.

In conclusion, the high catalytic activity and good stability of the catalyst observed for NaCl/Mn-oxide suggest that this is a promising catalyst for oxidative coupling of methane.

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References

1 G. E. Keller and M. M. Bhasin, *J. Catal.*, 1982, **73**, 9.

2 W. Hinsen, W. Bytyn, and M. Baerns, Proc. 8th Int. Congr. Catal., 1984, vol. 3, 581.

3 T. Ito, Ji-Xiang Wang, Chiu-Hsun Lin, and J. H. Lunsford, *J. Am. Chem. Soc.*, 1985, **107**, 5062.

4 (a) K. Otsuka, K. Jinno, and A. Morikawa, *Chem. Lett.*, 1985, 499; (b) K. Otsuka, Qin Liu, M. Hatano, and A. Morikawa, *ibid.*, 1986, 467; (c) K. Otsuka, Qin Liu, M. Hatano, and A. Morikawa, *ibid.*, 1986, 903; (d) K. Otsuka, Qin Liu, and A. Morikawa, *J. Chem. Soc., Chem. Commun.*, 1986, 586; (e) K. Otsuka, K. Jinno, and A. Morikawa, *J. Catal.*, 1986, **100**, 353.

5 H. Imai and T. Tagawa, *J. Chem. Soc., Chem. Commun.*, 1986, 52.

6 T. Moriyama, N. Takasaki, E. Iwamatsu, and K. Aika, *Chem. Lett.*, 1986, 1165; K. Aika, T. Moriyama, N. Takasaki, and E. Iwamatsu, *J. Chem. Soc., Chem. Commun.*, 1986, 1210.

7 K. Asami, S. Hashimoto, T. Shikada, K. Fujimoto, and H. Tominaga, *Chem. Lett.*, 1986, 1233.

8 U.S. Pat. 4,499,322(1985), 4,499,323(1985); WO 85/04821, WO 85/04867.