Beneficial Effect of Oxygen Distribution on Methane Conversion and C_2-Selectivity in Oxidative Coupling of Methane to C_2-Hydrocarbons over Lanthanum-promoted Magnesium Oxide

V. R. Choudhary,* S. T. Chaudhari, A. M. Rajput, and V. H. Rane

Chemical Engineering Division, National Chemical Laboratory, Pune—411 008, India

Distribution of oxygen feed throughout the catalyst causes a significant increase in both the conversion and selectivity for C_2-hydrocarbons in oxidative coupling of methane over La-promoted MgO.

Our recent studies[1,2] have revealed that La-promoted MgO[1] and CaO[2] catalysts show very high activity, C_2-selectivity, and C_2-space–time-yield with no catalyst deactivation in oxidative coupling of methane to C_2-hydrocarbons. We now report a new beneficial effect of distribution of oxygen feed on the methane conversion and C_2-selectivity in the oxidative coupling of methane over La-promoted MgO.

La-promoted MgO [La/Mg (mol/mol) = 0.1] catalyst was prepared by impregnating magnesium hydroxide (prepared by precipitation from aqueous magnesium nitrate by ammonium hydroxide) with a solution of lanthanum nitrate, drying, pressing, crushing to particles of 22—30 mesh size and calcining in air at 950 °C for 10 h. The catalytic reaction was carried out at atmospheric pressure in four tubular quartz

Table 1. Oxidative coupling of methane over La-promoted MgO catalyst in four reactors connected in series (50 mg of catalyst in each reactor).

	Methane flow rate/	Flow rate of oxygen/cm^3 min^{-1}				Overall CH_4/O_2	Overall GHSV[b]/	Conversion/%		C_2-Selectivity	C_2H_4/C_2H_6	C_2-Productivity/
T/°C[a]	cm^3 min^{-1}	Reactor-1	Reactor-2	Reactor-3	Reactor-4	O_2 ratio	h^{-1}	CH_4	O_2	/%	ratio	mol g^{-1} h^{-1}
Effect of CH_4/O_2 ratio												
800	134	66	—	—	—	2.0	51 360	27.9	73.8	43.3	7.7	0.19
800	150	50	—	—	—	3.0	51 360	26.5	95.2	49.8	2.9	0.23
800	165	35	—	—	—	4.7	51 360	21.7	99.1	63.8	1.7	0.26
800	178	22	—	—	—	8.0	51 360	15.1	93.2	74.4	0.8	0.23
Effect of O_2 distribution												
700	150	50	—	—	—	3.0	51 360	28.6	99.5	50.3	2.3	0.25
700	150	30	—	20	—	3.0	51 360	32.0	99.1	59.2	1.6	0.33
700	150	13	13	12	12	3.0	51 360	33.6	99.3	62.0	1.5	0.36
750	150	50	—	—	—	3.0	51 360	28.1	99.4	49.5	2.5	0.24
750	150	30	—	20	—	3.0	51 360	31.6	98.9	58.6	1.8	0.32
750	150	13	13	12	12	3.0	51 360	35.7	99.0	60.6	1.8	0.37
800	160	40	—	—	—	4.0	51 360	22.6	90.1	62.4	1.8	0.26
800	160	20	—	20	—	4.0	51 360	25.3	86.6	70.3	1.2	0.33
850	178	22	—	—	—	8.0	51 360	17.7	98.9	74.5	1.3	0.24
850	178	6	6	5	5	8.0	51 360	20.1	98.7	80.4	1.2	0.33
750	320	80	—	—	—	4.0	102 700	22.6	85.1	64.7	1.3	0.54
750	320	28	28	12	12	4.0	102 700	29.1	98.7	70.0	1.2	0.75
850	320	80	—	—	—	4.0	102 700	23.1	95.0	61.0	2.3	0.52
850	320	40	—	40	—	4.0	102 700	25.6	94.2	70.0	1.0	0.66

[a] Catalyst bed temperature in all the four reactors, controlled within 2—3 °C. [b] Gas hourly space velocity.

reactors (i.d.: 10 mm); each containing 50 mg of catalyst packed between quartz wool plugs. The reactors were connected in series. The temperatures in all the reactors were measured by Chromel–Alumel thermocouples located in the catalyst beds. The catalyst was pretreated *in situ* in a flow of N_2 (100 cm^3 min^{-1}) at 850 °C for 1 h. Pure methane was fed to the first reactor, whereas the total oxygen feed was distributed by introducing oxygen at the desired flow rate in the feed of each of the reactors. The catalyst bed temperature could be controlled within 2—3 °C. The effluent gases of the last reactor were analysed by an on-line gas chromatograph.

Results (Table 1) clearly indicate that higher CH_4/O_2 ratios lead to higher selectivity for C_2-hydrocarbons but lower conversions of methane and *vice versa*. However, because of the distribution of oxygen feed in the reactors (Table 1), both the conversion of methane and the selectivity for C_2-hydrocarbons (and consequently the C_2-yield, the C_2-productivity, and the concentration of C_2-hydrocarbons in the product stream) in the methane conversion process are increased markedly. The increase in the conversion and selectivity, however, depends on the distribution of O_2 in the reactors; a greater distribution leads to higher conversion and selectivity. With a methane-rich feed, a very high C_2-selectivity (>74%) could be achieved at higher temperatures (800—850 °C). Also, if the O_2 feed is distributed between the reactors, the reaction is carried out at lower oxygen concentration, which minimises explosion hazards.

In the oxidative coupling of methane over a number of catalysts, *viz.* Li–MgO,[3] Na–CaO,[4] Li–ZnO,[5] La_2O_3,[6] and La-promoted CaO,[2] an increase in the C_2-selectivity but decrease in the methane conversion with the increase in CH_4/O_2 ratio have also been observed. It is therefore expected that the distribution of O_2 will also be beneficial for achieving higher methane conversion and C_2-selectivity in the oxidative coupling of methane over these catalysts.

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