OXIDATIVE COUPLING OF METHANE TO C_2-HYDROCARBONS OVER La-PROMOTED CaO CATALYSTS

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Oxidative coupling of methane, lanthanum oxide promoted, calcium oxide catalyst for methane conversion.

La_2O_3 promoted CaO [La/Ca (mol/mol) = 0.05] catalyst shows very high activity and selectivity (methane conversion: 25%, C_2-selectivity: 66% and C_2-space-time-yield: 864 mmol $\cdot g^{-1}$ (cat.) $\cdot h^{-1}$) with no catalyst deactivation in oxidative coupling of methane to C_2-hydrocarbons at 800 ° C.

Earlier, calcium oxide promoted with alkali metals [1–3], alkaline earth metal halides [4] and barium oxide [5], as catalysts, for oxidative coupling of methane have been reported. The alkali metal [1] and metal halides [4] promoted catalysts were found to be deactivated during the catalytic process due to evaporation of the promoters. In this communication, we report our initial results on La_2O_3-promoted CaO catalysts showing much superior activity, selectivity, productivity or space-time-yield (STY) and stability (i.e. catalyst life) in the oxidative conversion of methane to C_2 hydrocarbons.

La_2O_3-CaO [La/Ca (mol/mol) = 0.001] to 0.2 catalysts were prepared by impregnating powdered CaO 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 surface area of the La_2O_3-CaO catalysts was in the range of 0.7 to 1.5 $m^2 \cdot g^{-1}$. The methane conversion reaction was carried out at atmospheric pressure in a conventional flow quartz reactor (i.d.: 10 mm) provided with a chromel-alumel thermocouple in the catalyst bed. The catalyst was pretreated in situ in the flow of N_2 (20 $cm^3 \cdot min^{-1}$) at 850 ° C for 1 h. The feed consists of only methane and oxygen ($CH_4/O_2 = 4$). The reactor effluent gases were analysed by an on-line gas chromatograph using Porapak-Q column.

Results on the oxidative coupling of methane over La_2O_3-CaO (La/Ca = 0 to ∞) catalysts are presented in table 1. Time-on-stream activity test for La-promoted CaO with La/Ca ratio of 0.05 was carried out at 800 ° C with space velocity of 1,45,600 $cm^3 \cdot g^{-1}$ (cat.) $\cdot h^{-1}$ for six days (table 1). No catalyst deactivation

Table 1
Results on oxidative coupling of methane to C_2-hydrocarbons over La_2O_3-CaO with different La/Ca ratios [feed gas composition: methane, 80 mol% and oxygen, 20 mol %]

La/Ca (mol/mol) ratio	Temp. (°C)	Space-velocity ($cm^3 \cdot g^{-1}$ (cat.)$\cdot h^{-1}$)	Total CH_4 conversion (%)	C_2-selectivity * (%)	$\frac{C_2H_4}{C_2H_6}$ ratio	C_2-STY (mmol$\cdot g^{-1}$ (cat.)$\cdot h^{-1}$)
0.0(CaO)	800	1,45,600	12.3	68.6	0.62	219
	850	1,45,600	19.7	70.8	1.04	363
0.001	800	1,45,600	20.2	64.4	0.91	338
	850	1,45,600	24.6	64.8	1.50	414
	800	2,95,000	21.7	63.6	1.00	727
0.005	800	1,45,600	22.7	66.8	1.06	394
	850	1,45,600	24.6	68.7	1.37	439
	800	2,95,000	22.7	66.8	1.10	801
0.02	800	1,45,600	22.4	62.0	0.98	361
	850	1,45,600	23.9	61.8	1.36	384
	800	2,95,000	21.7	64.1	1.10	732
0.05	800	1,45,600	24.0	68.0	0.95	424
	850	1,45,600	26.7	64.3	1.30	446
	800	2,95,000	25.1	65.6	1.20	864
0.2	800	1,45,600	25.7	65.9	1.13	440
	850	1,45,600	25.2	62.6	1.36	410
	800	2,95,000	24.2	68.2	1.40	795
$\infty(La_2O_3)$	800	1,45,600	23.6	63.1	1.30	386

* $C_2\text{-selectivity} = \left(\frac{\text{Conversion of methane to } C_2\text{-hydrocarbons}}{\text{Total conversion of methane}}\right) \times 100.$

was observed, which indicates a high catalyst stability in the methane conversion process.

The yield [total CH_4 conversion (%) × selectivity (%)/100] and productivity (or space-time-yield) of C_2-hydrocarbons obtained earlier over the CaO or lanthanum containing catalysts viz. Li-CaO [1], Na-CaO [3], $MgCl_2$-CaO [4], BaO-CaO [5] La_2O_3 [6] and $LaAlO_3$ [7] are as follows: C_2:-yield:- 13.2, 14.7, 7.0, 14.2, 4.4 and 12.2%, respectively, and C_2-STY:- 0.74, 0.56, 4.5, 20.9, 0.26, and about 10.9 mmol $\cdot g^{-1}$ (cat.)h^{-1}, respectively. A comparison of these results with the present results (table 1) shows that the performance of the La-promoted CaO catalysts in oxidative coupling of methane is very much superior to the previously reported catalysts. Further, the present catalysts contain high melting promoter (La_2O_3) and, therefore, catalyst deactivation due to evaporation of active component from the catalyst during the high temperature methane conversion process, as observed in the case of alkali metal and alkaline earth metal halide promoted CaO catalysts [1,4], is totally avoided. The present results on La_2O_3 (table 1) are also very much superior to those obtained earlier [6] and this suggests that the choice of process conditions, particularly feed composition and space velocity, is very important for

Table 2
Time-on-stream activity/selectivity of La_2O_3-CaO [La/Ca (mole/mole) = 0.05] in oxidative coupling of methane to C_2-hydrocarbons. (Reaction conditions-Temperature: 800 °C; feed gas composition: methane, 80 mol% and oxygen, 20 mol%; space velocity: 1,45,600 $cm^3 . g^{-1}$ (cat)·h^{-1})

Time-on-stream (h)	Total CH_4 conversion (%)	C_2-selectivity (%)
1.0	24.0	68.0
5.0	23.8	68.5
21.0	24.1	68.1
45.0	23.7	68.4
70.0	23.9	68.3
94.0	24.2	68.7
120.0	24.5	68.5
145.0	24.3	69.1

achieving high selectivity, yield and productivity of C_2-hydrocarbons in the oxidative coupling of methane.

In conclusion, the high catalytic activity and selectivity and excellent stability observed for La_2O_3-CaO suggest that this is a very promising catalyst for oxidative coupling of methane.

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