Oxidative Coupling of Methane over Alkaline Earth Promoted La_2O_3

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One wt% Sr/La_2O_3 is very active and selective for the oxidative coupling of methane, converting 1.2 mole g^{-1} h^{-1} of CH_4 with 72% selectivity into ethane and ethylene, at 750 °C, with 0.3 atm CH_4, 0.05 atm O_2, and 0.65 atm Ar.

The relative abundance of natural gas has spurred much research on catalytic process for converting methane into more valuable and more readily transportable hydrocarbons. The oxidative coupling of methane is one process which shows promise for transforming methane into ethylene.[1,2] We and others have found that a wide variety of oxides catalyse this reaction, with solid bases of the alkali, alkaline earth, and rare earth oxide groups exhibiting the highest activity and selectivity to C_2 hydrocarbons.[3—11] Here we report on the activity of promoted La_2O_3. Lanthanum oxide promoted with alkaline earth, in particular strontium, exhibits the highest activity and selectivity of the wide variety of promoted and unpromoted alkali, alkaline earth, and rare oxides we have tested.

Most of the metal oxides examined were obtained from the manufacturer and used without further modification, save pelletizing to between 32 and 50 mesh. The surface areas of

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Table 1. Activity and maximum selectivity of promoted La_2O_3 for the oxidative coupling of methane.[a]

		Selectivity (%)[c]					Conversion (%)		
Catalyst	T/°C[b]	C_2H_4	C_2H_6	Total C_n	CO	CO_2	O_2	CH_4	H_2/C_2[d]
La_2O_3	750	25.7	30.9	59.1	8.1	32.8	100[e]	19.6	1.1
1 wt% Li/La_2O_3	800	32.6	37.6	75.9	1.6	22.5	100	21.6	0.2
1 wt% Na/La_2O_3	800	31.4	33.2	69.2	2.4	28.4	100	20.0	0.4
1 wt% K/La_2O_3	800	30.1	30.3	64.0	7.7	28.3	100	20.6	0.8
1 wt% Mg/La_2O_3	750	28.0	32.1	65.4	8.5	26.1	100	20.7	0.7
1 wt% Ca/La_2O_3	750	28.6	31.1	64.3	9.4	26.3	100	19.4	0.8
1 wt% Sr/La_2O_3	750	28.7	34.9	69.0	4.8	26.2	100	20.9	0.6
1 wt% Ba/La_2O_3	800	30.5	33.6	68.1	3.2	28.7	100	20.3	0.5
1 wt% Pb/La_2O_3	750	24.9	33.2	60.6	3.5	35.9	100	18.5	0.5
1 wt% Bi/La_2O_3	750	27.0	34.6	65.2	2.1	32.7	100	18.4	0.3
1 wt% Ag/La_2O_3	800	27.8	31.9	62.8	5.4	31.8	100	20.0	0.7
Sm_2O_3	750	23.5	29.5	55.8	10.5	33.7	100	17.9	1.0
1 wt% Li/MgO	850	38.0	29.1	70.7	5.4	23.9	100	21.1	0.7
SrO	850	22.1	46.5	70.4	6.2	23.4	36	8.0	0.4
11.2 wt% Pb/SiO_2	900	27.2	31.0	60.0	11.8	28.2	50	8.5	0.2

[a] *Reaction conditions*: $P(CH_4)$ 0.30 atm; $P(O_2)$ 0.05 atm; P(Ar) 0.65 atm; g.h.s.v. 37 500 h^{-1} (N.T.P.) [b] Bed inlet temperature at maximum C_2 selectivity (900 °C highest temperature investigated). [c] Selectivity is based on moles CH_4 converted. [d] Molar ratio. [c] Oxygen material balance closed within ±5%.

Table 2. Comparison of promoted lanthanum oxide catalysts for the oxidative coupling of methane.[a]

		Selectivity (%)[b]					Conversion (%)			
Catalyst	Space velocity $/10^6 h^{-1}$	C_2H_4	C_2H_6	Total C_n	CO	CO_2	O_2	CH_4	Rate of CH_4 conversion $/mol\ g^{-1}\ h^{-1}$	H_2/C_2[c]
La_2O_3	3.40	15.6	49.9	69.8	17.2	13.0	29[d]	5.3	1.14	0.8
	1.20	21.5	45.9	71.1	14.9	14.0	66	10.8	0.82	0.6
1 wt% Li/La_2O_3	0.16	12.3	60.7	76.5	5.1	18.4	30	6.1	0.06	1.1
	0.05	19.0	54.3	78.7	2.8	18.5	57	11.4	0.04	0.3
1 wt% Sr/La_2O_3	3.40	11.4	58.2	75.4	10.7	13.9	34	5.6	1.20	0.6
	1.60	22.9	51.5	78.8	6.6	14.6	68	12.4	1.25	0.3

[a] *Reaction conditions*: bed inlet T 750 °C; $P(CH_4)$ 0.30 atm; $P(O_2)$ 0.05 atm; P(Ar) 0.65 atm. [b] Selectivity is based on moles CH_4 converted. [c] Molar ratio. [d] Oxygen material balance closed to within ±5%.

the oxides were usually less than 20 $m^2\ g^{-1}$. Lanthanum oxide was obtained from Union Molycorp and was 99.99% pure. Lanthanum oxide was promoted with 1 wt% of the other metals by incipient wetness impregnation of the nitrate salt of the metal. Impregnated samples were dried *in vacuo* at 110 °C for 12 h and calcined at 600 °C for 4 h. The 1 wt% Sr/La_2O_3 catalyst had an initial surface area of 3 $m^2\ g^{-1}$. The catalysts were tested in a 4 mm ID quartz tube at a bed inlet temperature of 500—900 °C, feed pressures of 0.30 atm CH_4, 0.05 atm O_2, and 0.65 atm Ar, and a gas hourly space velocity (g.h.s.v.) of 37 500 h^{-1} [normal temperature and pressure (N.T.P.)].

The results of the catalyst screening experiments are summarized in Table 1. Also included in the table for comparison are several metal oxides that previous researchers have shown to be active and selective for the oxidative coupling of methane (Sm_2O_3,[4] La_2O_3[5], Li/MgO,[5,6] SrO,[6] and Pb/SiO_2[2]). The data are reported for a reaction temperature where the catalyst exhibits maximum selectivity to ethane and ethylene per mole of methane converted. Sm_2O_3 and La_2O_3 are very similar catalysts for the oxidative coupling of methane. Both exhibit a maximum yield of C_2 product at 750 °C with about 24% selectivity for C_2H_4 and 30% selectivity for C_2H_6. In agreement with the findings of Otsuka *et al.*,[4] we found that the selectivities of nonacidic rare earth oxides, Y_2O_3, La_2O_3, Nd_2O_3, Sm_2O_3, Eu_2O_3, and Gd_2O_3, were nearly equal at the same reaction temperatures.[11] The screening tests did not distinguish activity differences among these catalysts, because all converted 100% of the O_2 feed at the space velocity chosen. The alkaline earth oxides, on the other hand, exhibit lower overall activity and a maximum C_2 selectivity at much higher temperatures than the rare earth oxides.[11] Strontium oxide exhibits very low activity, converting only 36% of the O_2 feed at 850 °C, and a g.h.s.v. of 37 500 h^{-1} (N.T.P.). The selectivity of MgO is improved by doping with alkali metals, in agreement with the results of Moriyama *et al.*[6] However, much higher temperatures are needed to achieve this selectivity than is observed for the rare earth oxide catalysts. Finally, 11.2 wt% Pb/SiO_2 gives reasonable selectivities to ethane and ethylene, but is relatively inactive, converting only 50% of the O_2 feed at 900 °C and a g.h.s.v. of 37 500 h^{-1} (N.T.P.).

Of the catalysts tested, the alkali and alkaline earth promoted La_2O_3 samples show the highest C_2 selectivity at the lowest reaction temperature. Selectivities for ethylene plus ethane can be improved 10% to 15% by addition of 1 wt% promoter. Lithium and strontium are particularly effective. To be able to distinguish the effects of the promoters on the activity of the rare oxide, higher space velocity experiments were conducted. The results of these are summarized in Table 2. Addition of lithium to La_2O_3 increases the C_2H_6 selectivity by 10% but decreases the rate of methane conversion twenty-fold. Addition of strontium increases the C_2H_6 selectivity by *ca.* 7% with no change in activity. The rate of CH_4 oxidation observed for La_2O_3 of 1.0 mol $g^{-1}\ h^{-1}$ (750 °C; 0.3 atm CH_4, 0.05 atm O_2, 0.65 atm Ar; space time 2 × 10^{-3}

g h l^{-1}) is in fair agreement with the rate of CH_4 oxidation observed by Otsuka *et al.*[4] for Sm_2O_3 (5.0 mol g^{-1} h^{-1} at 750 °C; 0.86 atm CH_4, 0.14 atm O_2; space time 2×10^{-4} g h l^{-1}).

It is remarkable that such a wide variety of oxides catalyse the oxidative coupling of methane with high activity and reasonable selectivity.[1—10] Our studies reveal that combinations of basic metal oxides of low redox potential, *i.e.* alkali, alkaline earth, and rare earth oxides excluding CeO_2 and Pr_6O_{11}, are selective for C_2 formation.[11] Of these, the rare earth oxides are the most active. Acidic metal oxides favour complete oxidation over coupling.

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