# Low temperature oxidative conversion of methane to synthesis gas over Co/rare earth oxide catalysts

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Received 9 July 1992; accepted 11 September 1992

CoO–rare earth oxide catalysts (particularly CoO–$Yb_2O_3$) show high activity and selectivity in the oxidative conversion of methane to CO and $H_2$ with very high productivity at low temperatures ( $\leqslant$ 700°C as low as 300°C).

**Keywords:** Methane; carbon monoxide; hydrogen; synthesis gas; Co/rare earth oxide catalysts; oxidation of methane to CO and $H_2$

Synthesis gas (i.e. a mixture of $H_2$ and CO, used as a feed stock for ammonia, methanol and Fischer–Tropsch synthesis processes) is produced from methane mostly by its steam reforming [1,2], which is highly energy intensive and also suffers from limitations like poor selectivity for CO and high $H_2/CO$ product ratio, unsuitable for methanol and Fischer–Tropsch synthesis. It can also be produced by the high pressure non-catalytic partial oxidation of methane [1,2], but although this process is mildly exothermic and also free from the above limitations, it operates at very high temperature ($\geqslant$ 1300°C). Because of the energy crises and need for the conversion of methane/natural gas into easily transportable and/or value added products (viz. methanol, liquid hydrocarbon fuels, etc.) [3–5], it is of great practical importance to develop a catalytic oxidative methane-to-synthesis gas conversion process operating at a much lower temperature, preferably below 600°C. Recently, a use of $Ln_2Ru_2O_7$ (Ln = lanthanide) [6] and $Eu_2Ir_2O_7$ [7] and $Ni/Al_2O_3$ [8] as catalysts, operating nearly at thermodynamic equilibrium at > 750°C and atmospheric pressure, for the methane oxidation process has been suggested. We report here our preliminary results disclosing the use of CoO–rare earth oxide catalysts, particularly

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Table 1
Oxidative conversion of methane to CO and $H_2$ over unreduced CoO–rare earth oxide (Co/rare earth mole ratio = 1.0) catalysts (feed: a mixture of 67 mol% $CH_4$ and 33 mol% $O_2$, GHSV (gas hourly space velocity at STP): $5.2 \times 10^5$ $cm^3$ $g^{-1}$ $h^{-1}$, pressure: 1.0 atm).

| Catalyst | Temp. (°C) | $CH_4$ conv. (%) | Selectivity (%) | | $H_2$/CO ratio | CO STY [a] (mol $g^{-1}$ $h^{-1}$) |
|---|---|---|---|---|---|---|
| | | | CO | $H_2$ | | |
| CoO–$CeO_2$ | 700 | 48.5 | 77.0 | 69.1 | 1.79 | 5.8 |
| | 500 | 35.4 | 61.3 | 64.8 | 1.80 | 5.3 |
| CoO–$Nd_2O_3$ | 700 | 64.0 | 88.5 | 82.8 | 1.87 | 8.7 |
| | 500 | 56.3 | 82.9 | 76.0 | 1.83 | 7.2 |
| | 350 | 48.1 | 76.3 | 66.3 | 1.74 | 5.7 |
| CoO–$Sm_2O_3$ | 700 | 52.8 | 86.6 | 71.2 | 1.64 | 7.1 |
| | 600 | 47.7 | 82.0 | 65.8 | 1.60 | 6.0 |
| | 500 | 48.3 | 80.1 | 62.3 | 1.56 | 6.0 |
| | 350 | 43.5 | 74.3 | 59.8 | 1.61 | 5.0 |
| CoO–$Eu_2O_3$ | 700 | 61.9 | 88.8 | 84.8 | 1.91 | 8.5 |
| | 600 | 58.5 | 86.3 | 82.4 | 1.91 | 7.8 |
| | 500 | 53.7 | 82.6 | 80.4 | 1.95 | 6.8 |
| | 300 | 46.4 | 73.3 | 69.6 | 1.90 | 5.2 |
| CoO–$Yb_2O_3$ | 700 | 79.2 | 90.0 | 88.4 | 1.97 | 11.2 |
| | 600 | 72.6 | 87.2 | 86.1 | 1.97 | 9.8 |
| | 500 | 70.4 | 83.1 | 83.2 | 2.00 | 9.0 |
| | 400 | 64.6 | 80.0 | 80.1 | 2.00 | 7.9 |
| CoO–$Yb_2O_3$ [b] | 800 | 79.0 | 95.5 | 92.3 | 1.93 | 11.6 |
| | 700 | 74.0 | 92.5 | 91.5 | 1.98 | 10.6 |
| | 500 | 65.0 | 86.2 | 86.2 | 2.00 | 8.6 |
| | 300 | 59.4 | 80.3 | 80.3 | 2.00 | 7.4 |

[a] Space-time-yield (or productivity).
[b] Reduced catalyst.

CoO–$Yb_2O_3$, which is not only highly active and selective and much more productive but also operates at much lower temperatures ($\leqslant$ 700°C, as low as 300°C) and far away from the thermodynamic equilibrium, in the oxidative conversion of methane to CO and $H_2$.

The CoO–rare earth oxide catalysts (table 1) were prepared by decomposing a finely ground mixture of cobalt nitrate and rare earth oxide in air at 600°C for 4 h, then powdering the resulting mass, pressing binder-free and crushing to 22–30 mesh size particles and finally calcining in air at 900°C for 6 h. The catalytic reactions were carried out in a quartz microreactor (i.d. 4 mm) containing 20 mg catalyst. The reaction temperature was measured by a chromel–alumel thermocouple located in the catalyst bed. The oxidative methane conversion reaction was carried out over the catalyst with or without its reduction by $H_2$ at 500°C in a flow (80 $cm^3$ $min^{-1}$) of $H_2$–$N_2$ mixture (20 mol% $H_2$) for 1 h. The water formed in the reaction was measured by condensing it from the product gases at 0°C. The feed and product gases (viz. $CH_4$, $O_2$, CO, $CO_2$, and $H_2$) were analysed by an on-line gas chromatograph using a spherocarb column. There was no formation of $C_{2+}$ products; the conversion of oxygen in the reaction was almost 100%. The $H_2$ and CO selectivities were based on both products formed and methane reacted.

Among the CoO–rare earth oxide catalysts (table 1), the CoO–$Yb_2O_3$ showed the best performance in the oxidative conversion of methane, according to the reaction

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 + 5.4\ \mathrm{kcal/mol(CH_4)}.$$

The results reveal that, by using the CoO–$Yb_2O_3$ catalyst, it is possible to obtain synthesis gas with $H_2$/CO ratio of about 2.0 (which is required for methanol and Fischer–Tropsch synthesis) at high conversion and selectivity and very high productivity (or space-time-yield) by oxidative conversion of methane at $\leqslant$ 700°C (even at 300°C) and extremely high space velocity ($5 \times 10^5$ $cm^3$ $g^{-1}$ $h^{-1}$), which are 2–3 and 1–3 orders of magnitude of that used in the steam reforming process [1] and the partial oxidation of methane over the $Ln_2Ru_2O_7$ [6] and Ni/$Al_2O_3$ [8] catalysts, respectively. The reduced catalyst showed no significant change in its activity and selectivity when on the time-on-stream (at 700°C) for 15 h. The catalyst may or may not be reduced by $H_2$ before carrying out the methane oxidation reaction. However, the unreduced catalyst shows activity in the reaction only above 500°C; the catalyst is reduced by the $H_2$ formed in the reaction at $\geqslant$ 500°C and then shows the activity in the reaction at $<$ 500°C. The catalyst in its active form seems to be Co and/or partially reduced CoO dispersed on the rare earth oxide.

The selectivity for CO and $H_2$ is decreased with decreasing temperature. However, the selectivity at lower temperatures is very much higher than that expected according to the thermodynamic equilibrium, which favours the formation of CO and $H_2$ over $CO_2$ and $H_2O$ in the reaction only above 700°C [6,8]. This fact reveals that the formation of CO and $H_2$ at $<$ 700°C is kinetically controlled.

The conversion of methane in its reaction with water or $CO_2$ (feed: 50 mol% $CH_4$ and 50 mol% $H_2O$ or $CO_2$, GHSV: $5.2 \times 10^5$ $cm^3$ $g^{-1}$ $h^{-1}$ over the reduced CoO–$Yb_2O_3$ at $\leqslant$ 700°C was negligibly small (0.5%). This suggests that the reaction path for the present catalytic oxidative conversion process is completely different from that (which involves a sequence of following reactions: combustion of a part of methane to $CO_2$ and $H_2O$ with complete oxygen conversion, followed by the steam and $CO_2$ reforming of unconverted methane, and the shift and reverse shift reactions) considered for the high temperature non-catalytic process [1] and the earlier catalytic processes [6–8] operating at $>$ 750°C. However, in the present case, synthesis gas seems to be formed more directly. Further work is necessary for understanding the reaction path and mechanism.

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