Low-temperature total oxidation of methane over Ag-doped $LaMO_3$ perovskite oxides

V. R. Choudhary,* B. S. Uphade, S. G. Pataskar and G. A. Thite

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

Partial substitution of La by Ag, instead of Sr, in $LaMO_3$ (M = Co, Mn, Ni) perovskite causes a large increase in the catalytic activity of the perovskite in the complete combustion of dilute methane for its emission control, at low temperature (< 700 °C) and high space velocity (51 000 $cm^3\ g^{-1}\ h^{-1}$); Ag-doped $LaCoO_3$ shows the highest methane combustion activity.

Methane has a 20–30 times larger greenhouse effect relative to carbon dioxide. Hence, the control of methane emission from natural gas engines/power plants and petroleum and industries is essential. However, since methane is the most inert among the hydrocarbons, its oxidative destruction by complete combustion to CO_2 is difficult. Because of the scarcity and high cost of noble metals, worldwide efforts are being made to replace noble-metal catalysts (which show high methane combustion activity at low temperature) by non-noble metal catalysts, particularly ABO_3 type perovskite oxides (A = rare earth, B = transition metal such as Cr, Mn, Fe, Co, Ni *etc*) with or without partial substitution of A by other elements (*e.g.* Sr).[1–8] Earlier studies[3,5] showed that $LaMO_3$ (M = Co, Mn, Ni, Fe) and Sr-doped $LaCoO_3$ and $LaMnO_3$ perovskite oxides have high methane combustion activity. We report here our preliminary results showing a large increase in the methane combustion activity (< 700 °C and space velocity = 51 000 $cm^3\ g^{-1}\ h^{-1}$) of $LaMO_3$ (M = Mn, Co, Ni) perovskites due to the partial substitution of La by Ag instead of Sr; the highest methane combustion activity is shown by $La_{0.7}Ag_{0.3}CoO_3$ perovskite.

The $LaMO_3$ and $La_{0.7}Sr$ (or $Ag)_{0.3}MO_3$ (M = Mn, Co, Ni) perovskite oxides were prepared by coprecipitating mixed-metal carbonates of La and transition metal (*viz.* Mn, Co, Ni) with or without Sr or Ag from their mixed-nitrate solution with sodium carbonate, ageing the precipitate for 12 h, filtering and washing thoroughly with deionized water, drying (at 100 °C overnight), decomposing at 500 °C under static air for 5 h, powdering, washing with boiling deionized water to remove traces of sodium, again filtering and drying (at 100 °C overnight) pelletizing and calcining at 750 °C (for Ag containing perovskites) or 900 °C (for other perovskites) for 6 h under static air and crushing the calcined pellets to 22–30 mesh size particles. The perovskite oxide structure of all the catalysts was confirmed by XRD. The methane combustion activity of the catalysts was determined at atmospheric pressure in a continuous fixed-bed quartz microreactor (i.d. = 10 mm) packed with 0.1 g catalyst (particle size = 22–30 mesh) mixed uniformly, with 0.9 g inert α-Al_2O_3 particles, at different temperatures using 4 mol% methane in air as a feed at a space velocity (measured at 0 °C and 1 atm pressure) of 51 000 $cm^3\ g^{-1}\ h^{-1}$. The reaction temperature was measured by a chromel-alumel thermocouple placed in the centre of the catalyst bed. The products (after condensing the water from the product stream at 0 °C) were analysed by an on-line GC using a Spherocarb column. The temperature programmed reactions of methane (in the absence of free O_2) over the catalysts were carried out in a quartz reactor. The products were sampled at different temperatures using a multiloop gas-sampling valve and analysed by GC. The pulse reaction of pure methane (in the absence of free O_2) over the catalyst was carried out at 550 °C in a quartz-pulse microreactor connected to a GC, described earlier,[9] using He as a carrier gas. In both the presence and absence of free O_2, the combustion of methane over the catalysts was complete with no formation of CO.

Results in Table 1 reveal that the reaction temperature required for 50 and 90% methane conversion is reduced markedly when La is partially substituted by Ag, instead of Sr, in the $LaMnO_3$, $LaCoO_3$ and $LaNiO_3$ perovskites. Among the perovskite oxide catalysts, Ag-doped $LaCoO_3$ shows the highest methane combustion activity. It shows no sign of deactivation in the catalytic process when tested for 50 h at 600 °C.

In the absence of free O_2, a high conversion of methane is observed in the pulse-reaction of pure methane over the Ag-doped $LaCoO_3$ catalyst at 550 °C (Table 2). The conversion is descreased upon increasing the number of pulses and is reduced to a very low value after the 30th pulse. However, the initial high conversion is regained after reoxidation of the catalyst by O_2. This reveals the involvement of lattice oxygen in a redox mechanism in the methane combustion over the catalyst. The observed higher conversion, after reoxidation, for the initial 15 pulses may be due to chemisorbed oxygen on the catalyst.

Results of the temperature programmed reaction of methane over the $LaCoO_3$ and Sr- and Ag-doped $LaCoO_3$ catalysts in the

Table 1 Results of complete combustion of methane over different perovskite oxide catalysts

Catalyst	Reaction temperature/°C	
	50% conv.	90% conv.
$LaMnO_3$	693	793
$La_{0.7}Sr_{0.3}MnO_3$	670	760
$La_{0.7}Ag_{0.3}MnO_3$	592	683
$LaCoO_3$	634	743
$La_{0.7}Sr_{0.3}CoO_3$	637	753
$La_{0.7}Ag_{0.3}CoO_3$	560	653
$LaNiO_3$	793	$\gg$800
$La_{0.7}Sr_{0.3}NiO_3$	620	740
$La_{0.7}Ag_{0.3}NiO_3$	580	673

Table 2 Pulse reaction of pure methane over $La_{0.7}Ag_{0.3}CoO_3$ at 550 °C in the absence of free O_2 [amount of catalyst, 0.1 g; pulse, pure methane (0.2 cm^3); carrier gas, He (30 $cm^3\ min^{-1}$)]

Pulse number	Methane conv. (%)	
	Fresh catalyst	Reoxidised catalyst[a]
1	24.0	37.8
2	23.1	26.0
5	19.8	20.0
10	13.8	14.3
15	9.9	10.5
20	6.5	6.5
25	4.8	4.7
30	1.1	1.2

[a] After the 30th pulse the catalyst was pretreated in O_2 at 550 °C for 1 h.

absence of free O_2 (Fig. 1) clearly show that the lattice oxygen of Ag-doped $LaCoO_3$ is much more reactive at lower temperatures than that of $LaCoO_3$ and Sr-doped $LaCoO_3$ catalysts. Because of the higher reactivity of lattice oxygen, the Ag-doped $LaCoO_3$ is catalytically more active in the methane combustion at lower temperatures.

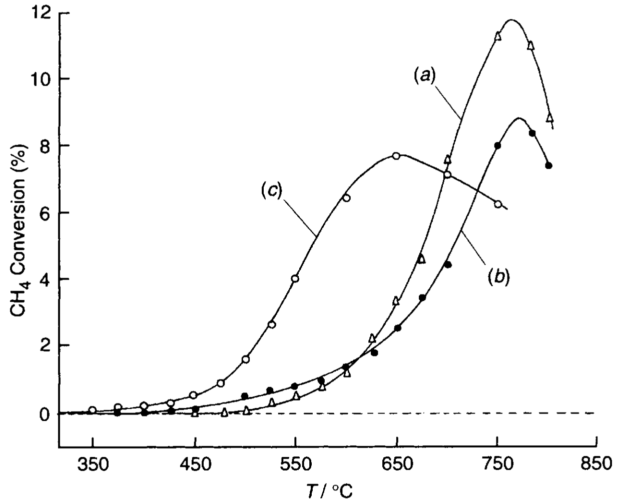

Fig 1 Temperature programmed reaction of methane over $LaCoO_3$ (*a*), $La_{0.7}Sr_{0.3}CoO_3$ (*b*) and $La_{0.7}Ag_{0.3}CoO_3$ (*c*) in the absence of free O_2 [amount of catalyst, 0.5 g; feed, 5 mol% CH_4 in He (100 cm^3 min^{-1}); linear heating rate, 20 °C min^{-1}]

In conclusion, the partial substitution of La by Ag, instead of Sr, in $LaMO_3$ (M = Mn, Co, Ni) perovskites results in a large increase in their methane combustion activity at lower temperatures due to the increase in the reactivity of their lattice oxygen. The Ag-doped $LaCoO_3$ is a highly promising catalyst for the complete combustion of methane for its emission control.

References

1 L. G. Tejuca, J. L. G. Fierro and J. M. D. Tascon, *Adv. Catal.*, 1989, **36**, 237.

2 T. Seiyama, *Catal. Rev. Sci. Eng.*, 1992, **34**, 281.

3 H. Arai, T. Yamada, K. Eguchi and T. Seiyama, *Appl. Catal.*, 1986, **26**, 265.

4 H. M. Zhang, Y. Teraoka and N. Yamazoe, *Catal. Today*, 1989, **6**, 155.

5 J. G. McCarty and H. Wise, *Catal. Today*, 1990, **8**, 231.

6 B. de Collongue, E. Garbbowski and M. Primet, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 2493.

7 P. E. Marti and A. Baiker, *Catal. Lett.*, 1994, **26**, 71.

8 P. E. Marti, M. Maciejewski and A. Baiker, *Appl. Catal. B: Environ.*, 1994, **4**, 225.

9 V. R. Choudhary and V. H. Rane, *J. Catal.*, 1992, **135**, 310.

Received, 20th December 1995; Com. 5/08394J