

Highly Stable Li-doped Magnesium Oxide Catalyst for Oxidative Conversion of Methane to Higher Hydrocarbons

V. R. Choudhary,* S. T. Chaudhari and M. Y. Pandit

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

A Li-doped MgO catalyst, when prepared by impregnation of magnesium acetate with aqueous lithium acetate (with a Li to Mg molar ratio of 0.1 : 1) followed by calcination in air at 750 °C, shows no change in its initial high activity and selectivity in oxidative conversion of methane to higher hydrocarbons, for a long period.

Li-MgO^{1,2} shows high catalytic activity and selectivity in oxidative conversion of methane (OCM) to C₂ and higher hydrocarbons. However, earlier studies²⁻⁶ indicated that Li-MgO is deactivated rapidly in the initial short period of the OCM process owing to sintering and/or loss of Li by evaporation. This limits the practical use of Li-MgO as a catalyst in the OCM process. We now report our results on Li-doped MgO, prepared using magnesium acetate and lithium acetate as precursors for MgO and Li, respectively, showing high CO₂ content, high CO₂ chemisorption and also high stability for catalytic activity and selectivity in the OCM process for a long period.

Li-MgO catalysts were prepared by impregnating powdered magnesium acetate with aqueous lithium acetate (Li:Mg molar ratio 0.02-0.5:1), drying, decomposition (or calcination) in air at 750 °C for 6 h, powdering, pressing and crushing to 22-30 mesh size particles. The CO₂ content of the catalysts was determined by measuring the CO₂ evolved by heating the catalyst (pretreated *in situ* in N₂ at 750 °C for 1 h)

from 750 to 1000 °C. The chemisorption of CO₂ on the catalysts (at 150 and 500 °C), measuring their basicity, was determined by the thermal desorption method described earlier.⁷ The OCM reaction on the catalysts was carried out at atmospheric pressure in a conventional flow quartz reactor (i.d.: 10 mm) packed with 0.5 g of catalyst. The catalyst was pretreated *in situ* in a flow (25 cm³ min⁻¹) of N₂, O₂ or CO₂ at 750 °C for 1 h. The feed was a mixture of pure methane and oxygen. The product gases were analysed by an on-line gas chromatograph.

Results in Fig. 1 show no significant change in both the initial high activity and selectivity of the Li-MgO in the OCM process, indicating no catalyst deactivation with the process time. Also, the gas atmosphere (N₂, O₂ or CO₂) used in the catalyst pretreatment shows almost no influence on the initial catalytic activity or selectivity and the time-on-stream activity or selectivity. In contrast, in the earlier studies²⁻⁶ Li-MgO showed continuous deactivation at a high rate in an initial short period of the process.

Table 1 Properties of Li-doped MgO catalysts with different Li/Mg ratios and their activity and selectivity in oxidative conversion of methane to a higher hydrocarbons^a

Li/Mg	Surface area/ m ² g ⁻¹	CO ₂ content/ mmol g ⁻¹	CO ₂ chemisorbed/mmol g ⁻¹		CH ₄ con- version (%)	Selectivity (%)		C ₂₋₄ yield (%)
			150 °C	500 °C		C ₂	C ₂₋₄	
0.02	9.5	<0.01	0.34	0.13	9.2	45.6	50.0	4.6
0.05	8.1	0.16	0.62	0.32	17.8	67.0	75.2	13.4
0.10	5.0	0.43	0.65	0.53	20.0	70.4	78.8	15.8
0.25	3.9	0.47	0.77	0.71	11.1	73.8	80.1	8.9
0.50	2.0	1.03	1.36	1.30	10.9	58.8	66.0	7.2
Empty reactor	—	—	—	—	No reaction			

^a Reaction temperature, 750 ± 2 °C; feed, 89 mol% CH₄ and 11 mol% O₂; space velocity, 20 540 cm³ (at STP) g⁻¹ h⁻¹; catalysts pretreated *in situ* in flowing of N₂ at 750 °C for 1 h.

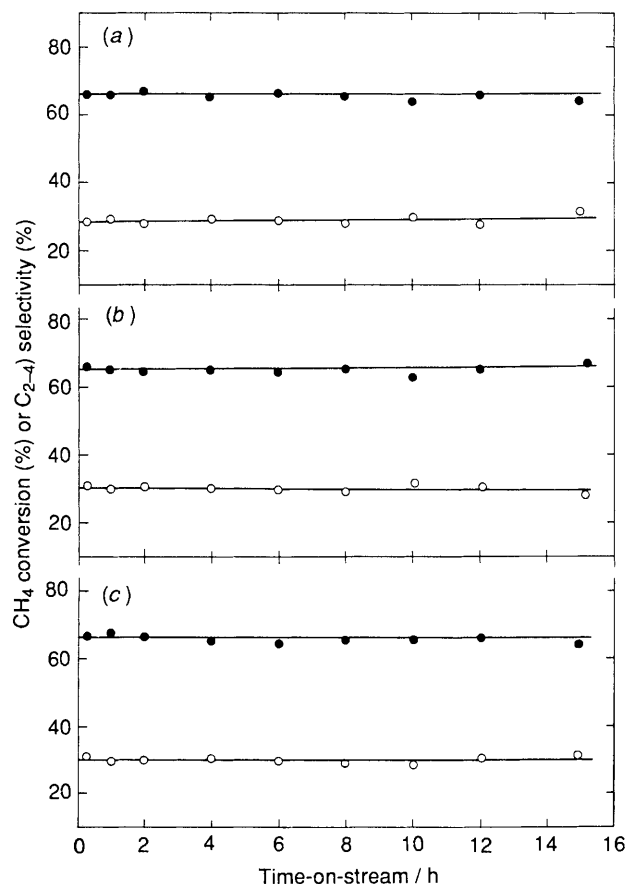


Fig. 1 Time-on-stream activity and selectivity of Li-doped MgO (Li/Mg = 0.1) in oxidative conversion of methane to higher hydrocarbons [at 750 °C; feed: 80 mol% CH₄ and 20 mol% O₂; space velocity, 10 270 cm³ (at STP) g⁻¹ h⁻¹], (a) catalyst pretreated *in situ* at 750 °C in N₂ flow for 1 h, (b) catalyst pretreated *in situ* at 750 °C in O₂ flow for 1 h and (c) catalyst pretreated *in situ* at 750 °C in CO₂ flow for 1 h (○, CH₄ conversion; ●, C₂₋₄ selectivity)

Results in Table 1 show a decrease in the surface area and an increase in the CO₂ content and the CO₂ chemisorption (at 150 and 500 °C) with increasing Li/Mg ratio of the catalyst. The best performance is, however, shown by the catalyst with Li/Mg = 0.1, indicating a detrimental effect of the higher CO₂ content on the catalytic activity mostly due to poisoning (or blocking) of strong basic sites on the catalyst by CO₂. The basicity of the Li-MgO catalysts (Table 1), measured by the chemisorption of CO₂, is much higher than that of other catalysts⁸ used for the OCM process.

The high stability for catalytic activity and selectivity in the OCM process shown by the present Li-MgO catalyst is attributed mostly to its high CO₂ content, which stabilises the catalyst against sintering and loss of Li during the process. This is consistent with the earlier observation^{5,9} indicating an increase in the stability of Li-MgO due to addition of CO₂ at low concentration in the reaction mixture.

Received, 19th April 1991; Com. 1/01847G

References

- 1 T. Ito and J. H. Lunsford, *Nature*, 1985, **314**, 721.
- 2 T. Ito, J. X. Wang, C. H. Lin and J. H. Lunsford, *J. Am. Chem. Soc.*, 1985, **107**, 5062.
- 3 V. R. Choudhary, D. B. Akolekar and A. M. Rajput, in *Recent Trends in Chemical Engineering*, eds. B. D. Kulkarni, R. A. Mashelkar and M. M. Sharma, Wiley Eastern Ltd., New Delhi, 1987, vol. 1, p. 90.
- 4 C. Mirodatos, V. Perrichon, M. C. Durupt and P. Moral, in *Catalyst Deactivation*, eds. B. Delmon and G. F. Froment, Elsevier, Amsterdam, 1987, p. 183.
- 5 S. J. Korf, J. A. Roos, N. A. DeBruijn, J. G. Van Ommen and J. R. H. Ross, *J. Chem. Soc., Chem. Commun.*, 1987, 1433.
- 6 G. A. Martin, P. Turler, V. Ducarme, C. Mirodatos and M. Pinabiau, *Catal. Today*, 1990, **6**, 373.
- 7 V. R. Choudhary and V. H. Rane, *Catal. Lett.*, 1990, **4**, 101.
- 8 V. R. Choudhary, V. H. Rane and S. T. Chaudhari, *Catal. Lett.*, 1990, **6**, 95.
- 9 S. J. Korf, J. A. Roos, N. A. deBruijn, J. G. Van Ommen and J. R. H. Ross, *Appl. Catal.*, 1990, **58**, 131.