Selective Oxidation of Methane in the Presence of NO: New Evidence on the Reaction Mechanism

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Partial oxidation of methane in the presence of nitric oxide using Li/MgO as catalyst demonstrates that at least two oxidising species/sites are significant for this catalyst system.

The oxidative coupling of methane to form ethene and ethane remains a subject of considerable current research interest. Initially recent studies of this reaction concentrated on the identification of suitable catalysts and consequently a considerable number of catalyst formulations have been evaluated, including alkaline earth oxides,[1,2] rare earth oxides,[3,4] single transition metal oxides,[5,6] and more complex oxides.[7,8] In general most of these formulations give similar product distributions, but in terms of catalyst activity lithium carbonate promoted MgO, the catalyst originally identified by Lunsford,[1] remains one of the most effective formulations and is currently being evaluated at pilot plant scale.[9] More recently attention has been focused on understanding the mechanism of this reaction on Li/MgO and there is general agreement[10] that methyl radicals are generated *via* a rate-determining[11] hydrogen atom abstraction from methane by $O^-_{(s)}$, which subsequently dimerise to ethane or react with molecular oxygen to give non-selective oxidation products. We have previously demonstrated[12] using N_2O as oxidant that $O^-_{(s)}$ has two distinct roles in the oxidation of methane, one selective and one non-selective, but to date studies have not determined if other oxidising species or sites are also significant with the Li/MgO catalyst. We have now addressed this question, and in this communication we discuss the results of methane partial oxidation in the presence of nitric oxide, a stable π radical and known radical scavenger,[13] which demonstrate that a second oxidising species is also significant.

The 5% Li/MgO catalyst was prepared as previously described,[12] and reactions were performed in a quartz microreactor (13 mm o.d.) at 650 °C. CH_4/O_2 and CH_4/N_2O mixtures were individually reacted over the catalyst (4 ml) in the presence and absence of NO (2.5 mol % in N_2). Blank thermal reactions in the absence of catalyst were negligible under the conditions tested and also the reaction of $CH_4/NO/N_2$ did not give rise to any products indicating that under these conditions nitric oxide does not act as a radical initiator.

CH_4/N_2O (CH_4/N_2O = 3 molar ratio) was reacted over Li/MgO for 300 min (Figure 1) and a decrease in conversion to both C_2 and CO_2 products was observed which is due to a

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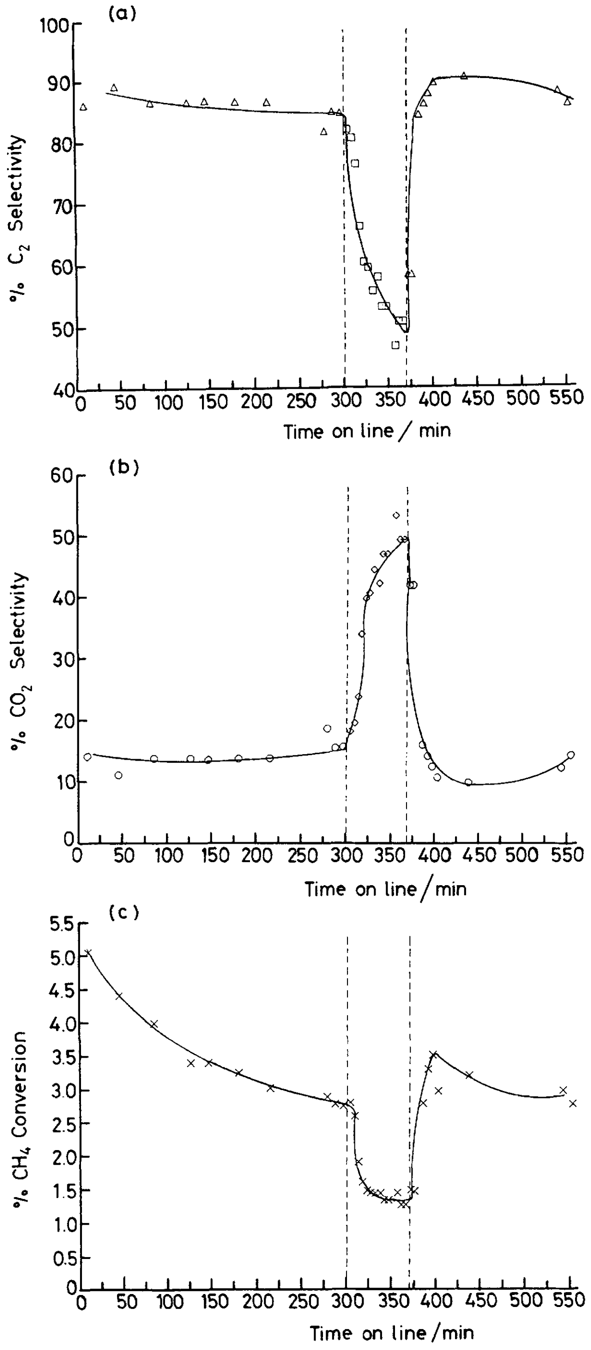

Figure 1. Effect of addition of NO for methane partial oxidation: (a) total C_2 selectivity, △ before/after NO addition, □ during NO addition; (b) CO_2 selectivity, ○ before/after NO addition, ◇ during NO addition; (c) CH_4 conversion.

combination of loss of surface area and lithium from the catalyst.[14] Addition of 2.5 mol % NO in N_2 to the reactants ($N_2O : NO = 52.5$ molar ratio) caused an immediate decrease in C_2 production with a concomitant increase in CO_2. On removal of NO/N_2 from the reactants, the production of C_2 hydrocarbons immediately increased whilst the CO_2 decreased. Significantly the C_2 production increased to a level much higher than that observed immediately preceding NO treatment of the catalyst before decreasing slowly to the expected level. In addition a similar but opposite trend is observed for CO_2 production. Similar trends were observed in the reaction of CH_4/O_2 and NO/N_2 mixtures over Li/MgO and in addition the effect could be observed in a number of reaction cycles involving the presence and absence of NO.

Since a number of previous studies[10] have demonstrated the importance of $O^-_{(s)}$ as radical initiators in this catalyst system the immediate effect observed on addition of NO is not in itself unexpected. Interaction of NO with $O^-_{(s)}$ could be expected to decrease the production of C_2 hydrocarbons and the concomitant increase in CO_2 merely reflects that the total oxidation of the methane becomes dominant in the absence of significant concentrations of $O^-_{(s)}$. However, the marked increase in C_2 production observed on removal of NO is considered to be of mechanistic importance. The increase in C_2 to levels higher than those observed immediately prior to NO addition indicates that, on removal of NO, the concentration of $O^-_{(s)}$ established from the oxidant must also therefore be higher than the corresponding level of $O^-_{(s)}$ prior to NO addition. The subsequent slower attainment of C_2 and CO_2 products to levels that are similar to those observed prior to NO addition is indicative that a second surface oxygen species, that is responsible for non-selective oxidation, is established more slowly than the selective oxidising species $O^-_{(s)}$. Hence the results of this study clearly indicate that at least two distinct oxidising species/site are significant on Li/MgO, only one of which is involved in selective C_2 hydrocarbon product formation. These results are of particular significance in the design of improved catalysts. Identification of the second oxidative species/site would enable catalysts to be prepared in which the formation of the non-selective species can be minimised.

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References

1 T. Ito and J. H. Lunsford, *Nature* (*London*), 1985, **314**, 721.
2 C.-H. Lin, J.-X. Wang, and J. H. Lunsford, *J. Catal.*, 1988, **111**, 302.
3 J. M. DeBoy and R. F. Hicks, *J. Chem. Soc., Chem. Commun.*, 1988, 982.
4 K. Otsuka and T. Komatsu, *Chem. Lett.*, 1987, 483; *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 1315.
5 G. E. Keller and M. M. Bhasin, *J. Catal.*, 1982, **73**, 9.
6 K. Otsuka and M. Hatano, in Proc. 1st Workshop on Catalytic Methane Conversion, Bochum 1988, to be published in *Catal. Today*.
7 H. Nagamoto, K. Amanuma, and H. Inoue, *Chem. Lett.*, 1988, 237.
8 J. M. Thomas, X. Zhang, and J. Stachurski, *J. Chem. Soc., Chem. Commun.*, 1988, 162.
9 J. H. Edwards and R. J. Tyler, in ref 6.
10 (a) J. H. Lunsford, C.-H. Lin, J.-X. Wang, and K. D. Campbell, in 'Microstructure and Properties of Catalysts,' eds. M. M. J. Treacy, J. M. Thomas, and J. M. White, Mat. Res. Soc. Symp. Proc., Vol. 3, Materials Research Soc., Pittsburgh, 1988, p. 305; (b) S. P. Mehandru, A. B. Anderson, and J. F. Bradzil, *J. Am. Chem. Soc.*, 1988, **110**, 1715; (c) D. J. Driscoll, W. Martir, J.-X. Wang, and J. H. Lunsford, *ibid.*, 1985, **107**, 58; (d) M. Anpo, M. Sunamoto, T. Doi, and I. Matsuura, *Chem. Lett.*, 1988, 701; (e) C. T. Au and M. W. Roberts, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 2047.
11 N. W. Cant, C. A. Lukey, P. F. Nelson, and R. J. Tyler, *J. Chem. Soc., Chem. Commun.*, 1988, 766.
12 G. J. Hutchings, M. S. Scurrell, and J. R. Woodhouse, *J. Chem. Soc., Chem. Commun.*, 1987, 1388.
13 R. A. Kenley and D. G. Hendry, *J. Am. Chem. Soc.*, 1982, **104**, 220.
14 G. J. Hutchings, M. S. Scurrell, and J. R. Woodhouse, *Stud. Surf. Sci. Catal.*, 1988, **36**, 415.