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OXIDATIVE COUPLING OF METHANE USING Li/MgO CATALYST: RE-APPRAISAL OF THE OPTIMUM LOADING OF Li

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The effect of the level of lithium carbonate doping on MgO, prepared by thermal decomposition of the basic carbonate, is re-examined. A low, sub monolayer, loading, ie. 0.2% Li_2CO_3-MgO is shown to significantly enhance both the specific activity for methane activation and the total C_2 hydrocarbon selectivity. The study indicates that the optimal loading of alkali promoters on MgO prepared in this way is considerably lower than indicated in previous studies.

1. Introduction

The investigation of catalysts for the oxidative coupling of methane has remained an area of intense study, since the catalysed reaction was first identified by Keller and Bhasin [1]. A large number of oxides have been shown to be effective catalysts including: alkaline earth oxides [2,3], rare earth oxides [4,5], oxyhalides [6] and complex oxides, eg. perovskites [7], and the relative efficacy of these materials have recently been reviewed [8]. However, by far the most research effort has been applied to understanding the mode of action of MgO and Li promoted MgO catalysts that were initially shown by Lunsford to be effective [2]. In a series of investigations Lunsford [9], using MgO prepared from commercial samples, demonstrated that for MgO a Li loading of ca 7% was optimal. Consequently, virtually all studies on Li/MgO catalysts carried out since the initial disclosures have utilised this or a similar lithium loading level.

More recently, there has been renewed interest in undoped MgO as it has been shown that the method of preparation is of crucial importance [10,11]. In

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particular, it has been shown that MgO prepared by thermal decomposition of the basic carbonate is most active and selective. Recent discussions [12], have noted that to achieve monolayer coverage of Li^+ on a typical MgO sample, a relatively low loading of ca 0.2% by mass is required. It is therefore apparent that the high loadings of lithium utilised in the catalytic studies will produce samples with many layers of lithium coverage. It is desirable to consider the role that lithium plays in the oxidative coupling of methane. Lunsford has proposed [9,13–15], that lithium establishes $[Li^+–O^-]$ centres on the surface of MgO and these are the active centres for methane activation. If such a hypothesis is valid then it would be expected that only a relatively low loading of lithium would be required to significantly enhance the specific catalytic activity, (ie. activity corrected for catalyst surface area after thermal treatment). Lunsford [9,13–15], has produced considerable e.s.r evidence in support of this proposal. A recent paper by Peng et al. [16], describes a surface investigation of Li/MgO catalysts which also concurs with the work of Lunsford, but data pertaining to specific catalytic activity was not presented in this study. Recently, Roos [17], has proposed that a possible alternative role of lithium would be to act in the gas phase, near the catalyst surface, as a radical trap and in this way the lithium would scavenge reactive intermediates involved in the non selective secondary oxidation of ethane and ethylene. If this hypothesis is valid then it could be expected that selectivity would increase with increasing lithium loading, but the overall activity would be expected to decrease, since the lithium would be expected to act as a non selective scavenger of reactive species. It could be expected that a high loading of lithium could be necessary to achieve an optimal effect. The aim of this paper is to reconsider the effect of lithium loading on MgO prepared using the optimal method of preparation (ie. decomposition of the basic carbonate). In particular, the purpose is to examine in detail a low loading level of lithium and to compare this to the lithium loading level utilised in most previous studies.

2. Experimental

MgO was prepared by the thermal decomposition of the basic carbonate (Merck) by a method previously described [18], and lithium doped samples (0.2%, 2.0% and 5.0% Li_2CO_3) were prepared by impregnation using an incipient wetness technique. An aqueous solution of Li_2CO_3 (Mallinckrodt) was added to MgO with stirring until the MgO was just completely wetted. The volume of solution required was 1.55 m/g for the sample of MgO used in these studies and the concentration of Li_2CO_3 was varied to obtain the required loadings of Li_2CO_3 in the final catalyst. The mixture was then dried at 140 ° C for 24 h. The catalysts were then ground, pelleted without the addition of binder and then sieved to give particles ca 0.5 mm. Catalysts were pretreated with oxygen (450 ° C, 1 h, 450 h^{-1}) in-situ in the reactor prior to catalyst testing. Similar results have also been obtained using preparation procedure in which MgO is suspended with stirring in an aqueous Li_2CO_3 solution, followed by evaporation of the excess liquid. Catalysts were evaluated for the methane coupling reaction in an all quartz microreactor, which has been previously described [19].

3. Results and discussion

The effect of the lithium loading on MgO (ex basic carbonate) was investigated at 700 °C and representative data are shown in table 1. It is apparent that as the general effect, as observed in the previous study of Lunsford [9], is that as the lithium loading is increased, the selectivity to C_2 hydrocarbons is enhanced at the expense of CO_2 and CO, while the overall conversion of methane and oxygen is decreased. It is important to note that for the Li/MgO catalysts the total C_2 selectivity observed at broadly similar reaction conditions only varied by ca 10%, whereas addition of only 0.2% lithium carbonate to MgO enhanced the C_2 selectivity by a factor of two. Hence, it is apparent that low, approximately monolayer [12], loadings of lithium can significantly influence selectivity. Increasing the loading of lithium to higher than monolayer coverage gives rise to a slight increase in selectivity, and in this study a broad maximum is observed below 5% loading.

In our previous studies [20], we demonstrated that addition of 5% lithium carbonate to MgO significantly affected the dependence of ethene and ethane selectivity on conversion when compared to that of undoped MgO. In particular, the ethene selectivities observed with the lithium doped catalyst were decreased relative to those of undoped MgO. The effect of lower loadings of lithium carbonate was therefore evaluated and the results (figs. 1 and 2) demonstrated that even a low loading (0.2% Li_2CO_3) significantly affects the dependence of C_2 hydrocarbon selectivity on increasing 1/GHSV. Comparable plots for MgO and 5% Li_2CO_3–MgO have been published by us previously [20]. These results therefore confirm that only relatively low loadings of lithium are required to observe the promotional effect on C_2 selectivity. A plot of total C_2 selectivity

Table 1
Product selectivities as a function of lithium carbonate loading on MgO [a]

Li %	GHSV h^{-1}	Conversion		Carbon product selectivity %				
		CH_4	O_2	CO_2	CO	C_2H_4	C_2H_6	Total C_2
0	1200	21.9	100	61.9	13.3	11.1	13.7	24.8
0.2	1132	29.8	94.2	38.3	2.9	17.3	41.5	58.8
2.0	1285	22.1	63.9	35.8	1.4	24.7	38.1	62.8
5.0	1319	11.8	27.8	43.7	3.3	16.2	36.8	53.0

[a] $CH_4/O_2 = 3$, 700 °C, 4 ml catalyst bed volume.

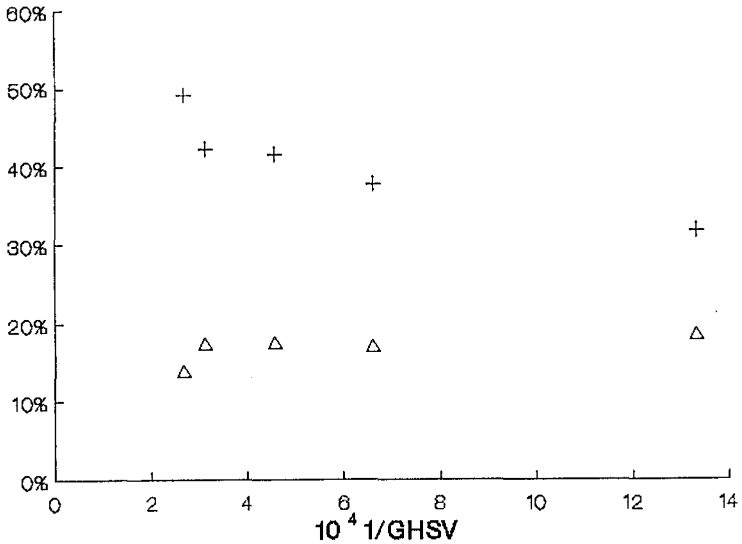

Fig. 1. Selectivity versus reciprocal space velocity for 0.2% Li_2CO_3–MgO catalyst with O_2 as oxidant at 700 °C. + C_2H_5; △ C_2H_4.

versus 1/GHSV at 700 °C for the four catalysts is shown in fig. 3, and from this it is apparent that, for these conditions, the 2% Li_2CO_3–MgO catalyst gives the highest selectivity to C_2 hydrocarbons at all conditions tested. However, this data further demonstrates the broad similarity in total C_2 selectivities for all the lithium doped samples when compared with the undoped MgO.

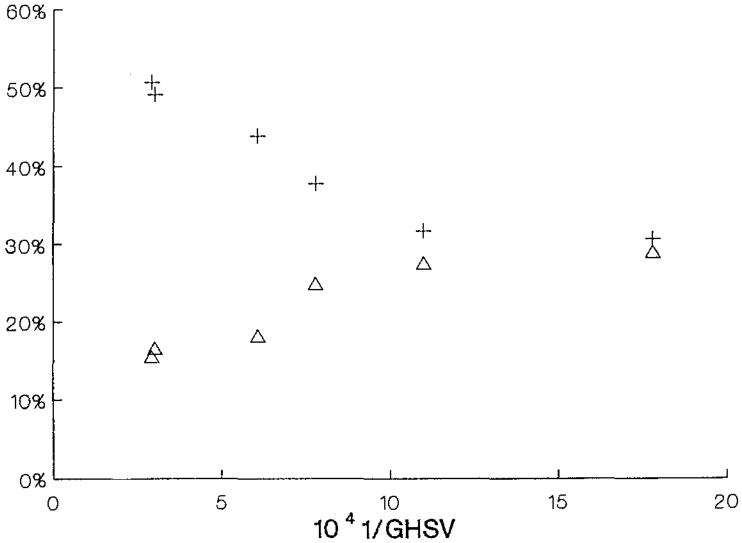

Fig. 2. Selectivity versus reciprocal space velocity for 2.0% Li_2CO_3–MgO catalyst with O_2 as oxidant at 700 °C. + C_2H_6; △ C_2H_4.

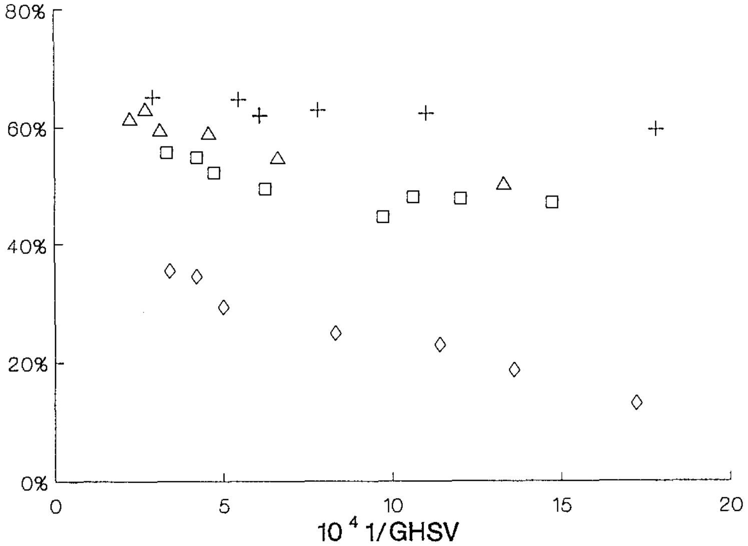

Fig. 3. Selectivity to total C_2 hydrocarbons versus reciprocal space velocity at 700 °C: ◇ MgO; △ 0.2% Li_2CO_3–MgO; + 2.0% Li_2CO_3–MgO; □ 5% Li_2CO_3–MgO.

It is tempting to use plots of selectivity versus reciprocal space velocity to obtain information concerning the nature of the primary products for the methane coupling reaction. In most cases, as exemplified by figs. 1 and 2, such plots indicate a positive intercept on the ordinate for both ethane and ethene, and from this one could conclude that both were primary hydrocarbon products. Indeed, in our early studies [20,21], we utilised these plots in this way. However, such plots cannot be considered definitive, since as we subsequently noted [19,22], the residence times utilised in such studies may still be too long to eliminate the contribution to selectivity made by rapid secondary reactions, particularly those that occur as gas phase reactions. Recently this point has been re-emphasised by Burch et al. [23], who has repreated the earlier studies using a commercial sample of undoped MgO. In general, the main problem associated with such plots is that the methane conversion is too high to make definite statements concerning primary products (eg. the lowest conversion in fig. 1 is 7.5% and the lowest conversion in the study of Burch et al. [23], is 3.6%). We have further addressed the nature of the primary products for the 5% Li_2CO_3–MgO catalyst system [19], and at very low conversion (ca 1–1.5%), it is found that significant selectivities of ethene (4%) are observed that are invariant with changes in the oxygen concentration (table 2), whereas the ethane selectivity markedly increased as the oxygen concentration decreased. At these low conversions and short contact times, if ethene were the product solely of secondary ethane conversion then variation in ethene selectivity would have been expected, and this is not observed. It can therefore be argued that such evidence supports the hypothesis that a small but

Table 2
Effect of CH_4/O_2 ratio on C_2 hydrocarbon selectivity over 5% Li_2CO_3–MgO, 710 °C, contact time = 0.05S

$CH_4:O_2$ Mole ratio	CH_4 conversion %	Selectivity %	
		C_2H_4	C_2H_6
3.0	1.8	4.3	47.5
5.2	1.5	3.2	57.1
10.5	1.0	4.3	71.0
21.0	1.3	4.7	68.8

significant primary selectivity for ethene exists for the lithium doped MgO catalysts.

Although the 2% Li_2CO_3–MgO catalyst gave a slightly enhanced selectivity when compared to the other lithium doped materials, the highest yield of C_2 hydrocarbons was observed with the lowest doping level (0.2% Li_2CO_3–MgO). Since it is known that addition of alkali metal compounds to MgO results in a decrease in surface area [8], it is instructive to consider the effect of lithium on the specific activity for methane activation (table 3). On this basis, it is apparent that addition of approximately a monolayer loading of lithium carbonate (0.2%) significantly enhances the specific activity for the formation of all reaction products, particularly ethene and ethane when the MgO is prepared via the thermal decomposition of the basic carbonate. It can therefore be concluded that the optimal loading of lithium with respect to catalytic activity is lower than that proposed in the earlier studies of Lunsford [9], whereas on the basis of total C_2 selectivity alone, it is clear that loadings of lithium carbonate between 0.2% and 5% give broadly similar results.

This study therefore emphasises the need to study alkali doped MgO catalysts at very low doping levels, since the desired promotional effects can all readily be observed. The need to study lower alkali loadings has also been shown in a recent study by Lunsford [24], when he demonstrated that the addition of 5% Li_2CO_3 to two MgO precursors with different morphologies resulted in final catalysts for which no detectable differences were observable using electron microscopy. It is

Table 3
Specific activity [a] data 700 °C, GHSV 1200 h^{-1}, $CH_4/O_2 = 3$

Catalyst	Surface area $m^2 \cdot g^{-1}$	10^4 specific activity/mol product $m^{-2}\ h^{-1}$				
		H_2	CO_2	CO	C_2H_4	C_2H_6
MgO	19	3.4	8.1	0.8	0.3	0.4
0.2% Li_2CO_3–MgO	6.5	6.2	10.3	0.5	2.4	5.7
5% Li_2CO_3–MgO	1.3	8.2	19.2	1.5	3.6	8.3

[a] Based on surface areas determined after reaction.

now essential that a detailed study of the effect of low loadings of lithium compounds on the structure of MgO should be carried out if a full understanding of the role of the lithium additive is to be determined. However, based on this initial study, the observation that very low lithium levels are effective is more consistent with the hypothesis of Lunsford [9,13–15], ie. that the lithium doping creates active sites for methane activation. The observation that the specific activity increases with addition of a very low loading of lithium carbonate provides evidence against the proposal of Roos [17], ie. that the lithium acts as a gas phase radical trap, since an opposite trend would have been expected.

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References

[1] G.E. Keller and M.M. Bhasin, J. Catal. 73 (1982) 9.

[2] T. Ito and J.H. Lunsford, Nature (London) 314 (1985) 721.

[3] C.H. Lin, J.-X. Wang and J.H. Lunsford, J. Catal. 111 (1988) 302.

[4] J.M. DeBoy and R.F. Hicks, J. Chem. Soc., Chem. Commun. (1988) 982.

[5] K. Otsuka and T. Komatsu, Chem. Lett. (1987) 843; J. Chem. Soc., Faraday Trans. 1, 83 (1987) 1315.

[6] W. Ueda and J.M. Thomas, J. Chem. Soc., Chem. Commun. (1988) 1148.

[7] H. Nagamoto, K. Amanuma and K. Inoue, Chem. Lett. (1988) 237.

[8] G.J. Hutchings, M.S. Scurrell and J.R. Woodhouse, Chem. Soc. Rev. 18 (1989) 251.

[9] T. Ito, J.-X. Wang, C-H Lin and J.H. Lunsford, J. Am. Chem Soc. 107 (1985) 5062.

[10] R.W. Joyner, Faraday Discussion, April 1989, Liverpool, Chem. Soc., 87 (1989) in press; J.S.J. Hargreaves, G.J. Hutchings and R.W. Joyner, Catal. Today, in press.

[11] J.A.S.P. Carreiro and M. Baerns, J. Catal. 117 (1989) 258.

[12] J. Cunningham, Faraday Discussion, Chem. Soc. 87 (1989) in press.

[13] D.J. Driscoll and J.H. Lunsford, J. Phys. Chem. 87 (1982) 301; 89 (1985) 4415.

[14] D.J. Driscoll, W. Martir, J.-X. Wang and J.H. Lunsford, in: *Adsorption and Catalysis on Oxide Surfaces*, eds. M. Che and G.C. Bond (Elsevier, Amsterdam, 1986) 403.

[15] J.H. Lunsford, Catal. Today, in press.

[16] X.D. Peng, D.A. Richards and P.C. Stair, J. Catal. 121 (1990) 99.

[17] J.A. Roos, PhD thesis, Catalytic activation of methane, University of Twente, 1989.

[18] M. Boudart, A. Delbouille, J.A. Dumesic, S. Khammonma and H. Topsoe, J. Catal. 37 (1975) 486.

[19] G.J. Hutchings, J.R. Woodhouse and M.S. Scurrell, J. Chem. Soc., Farad. Trans. 85 (1989) 2507.

[20] G.J. Hutchings, M.S. Scurrell and J.R. Woodhouse, J. Chem. Soc., Chem. Commun. (1987) 1862.

[21] G.J. Hutchings, M.S. Scurrell and J.R. Woodhouse, Catal. Today 4 (1989) 371.
[22] G.J. Hutchings, M.S. Scurrell and J.R. Woodhouse, *Proc. 9th Int. Congr. Catal.*, eds. M.J. Phillips and M. Ternan, 2 (Chemical Inst. Candada, 5, 1988) 335.
[23] R. Burch, A.A. Drost, D.A. Rice, S.C. Tsang and G. Webb, Cat. Lett. 3 (1989) 331.
[24] J.H. Lunsford, Faraday Discussion, Chem. Soc. 87 (1989) in press.