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Oxidative Coupling of Methane using Oxide Catalysts

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1 Introduction

In the past fifteen years there has been a resurgence in research into the production of chemicals and liquid transportation fuels from fossil fuel sources other than petroleum. This was largely spurred by the increased cost of petroleum and the majority of this effort was focused not only on improving the existing pathways based on the hydrogenation of carbon monoxide[1,2] but also led to the development of a new commercial process based on methanol conversion.[1,3,4] However, in recent years petroleum has again become inexpensive and this has significantly decreased the attention given to such research. In its place the research emphasis has now been directed at the utilization of natural gas as a source of chemicals and fuels. The reasons for this are twofold: first, the current reserves of natural gas are considered as a large underutilized energy resource, but a large proportion of these reserves are remotely located from high densities of consumers and chemical conversion of the methane is required to facilitate transportation. Second, vast quantities of natural gas are currently flared, particularly at locations where the gas is associated with crude oil, and consequently chemical conversion could be both economically and environmentally beneficial.

The conversion of natural gas *via* the process of partial oxidation to obtain more valuable chemical products, *e.g.* methanol and ethane, is not a new research topic. A large amount of pioneering research was completed in the 1920s and 1930s in which the partial oxidation reaction was investigated as a high pressure gas phase reaction, and this work has recently been reviewed by Gesser *et al.*[5] A

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[2] P. Biloen and W. H. Sachtler, *Adv. Catal.*, 1981, **31**, 165.

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small proportion of recent research effort has been focused on the production of methanol,[6,7] but to a large extent the identification of catalytic materials for this reaction has been unsuccessful. By far the majority of research has been carried out into the oxidative coupling of methane using oxide catalysts to form higher hydrocarbon products, mainly ethane and ethene. In 1988 three major scientific meetings[8] devoted over 60 papers solely to this reaction, which emphasizes the importance given to this topic at the present time. The aim of this review is to highlight the salient features of the recent research literature on the oxidative coupling of methane, particularly that published since 1986. In particular this review seeks to discuss the mechanism of methane oxidation over oxide catalysts and to consider experimental approaches that could enable the design of an improved catalyst.

2 Evaluation of Oxide Catalysts

A. Molecular Oxygen as Oxidant.—Initial work by Keller and Bhasin[9,10] considered that non-selective methane oxidation, either gas phase or catalysed, could be dominant when oxygen and methane were co-fed over a catalyst. To minimize such an effect they operated the reaction cyclically, *i.e.* methane and air were fed individually over the catalyst interspaced by a short purge of an inert gas. In this way methane was reacted with the catalyst which was stoicheiometrically reduced by the reaction, once all the readily reacted oxygen was depleted the reaction ceased. A range of oxides were identified which became active above 600 °C and produced ethene and ethane as major products. Of the oxides identified, supported manganese oxide was found to give the best results.

Later studies[11,12] demonstrated that cyclic operation was not necessary to obtain high selectivities, and in the presence of suitable catalysts co-fed methane and oxygen also gave high yields of C_2 hydrocarbons. Subsequently Lunsford[13] identified that lithium-promoted magnesium oxide could give a much improved catalytic performance. These early studies demonstrated that the oxidative coupling of methane to form C_2 hydrocarbons was a high temperature reaction and temperatures in excess of 600 °C were required to observe selective products (Figure 1). At lower temperatures only CO_2 and CO were observed as carbon-containing products. The early studies failed to observe that hydrogen was also a major reaction product, but subsequent studies noted that significant levels of hydrogen can be present.[14] In general, the products observed in the high

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[6] N. R. Foster, *Appl. Catal.*, 1985, **19**, 1.

[7] R. Pitchai and K. Klier, *Catal. Rev.-Sci. Eng.*, 1986, **28**, 13.

[8] First Workshop on the Catalytic Methane Conversion, May 1988, Bochum, *Catal. Today*, 1989, **4**, 271 500; *Proc. 9th Int. Cong. Catal.*, Calgary, ed. M. J. Phillips and M. Ternan, Chemical Institute of Canada, 1988, **2**, 883 997; Symposium on the Direct Conversion of Methane to Higher Hydrocarbons, Div. Pet. Chem., A.C.S. Symp. Ser., Los Angeles, September 1988.

[9] G. E. Keller and M. M. Bhasin, *J. Catal.*, 1982, **73**, 9.

[10] M. M. Bhasin, *Stud. Surf. Sci. Catal.*, 1988, **36**, 343.

[11] W. Hinsen and M. Baerns, *Chem. Ztg.*, 1983, **107**, 223.

[12] W. Hinsen, W. Bytyn, and M. Baerns, *Proc. 8th Int. Cong. Catal.*, Verlag Chemie, Weinheim, 1984, **3**, 581.

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

[14] G. J. Hutchings, M. S. Scurrell, and J. R. Woodhouse, *Appl. Catal.*, 1988, **38**, 157.

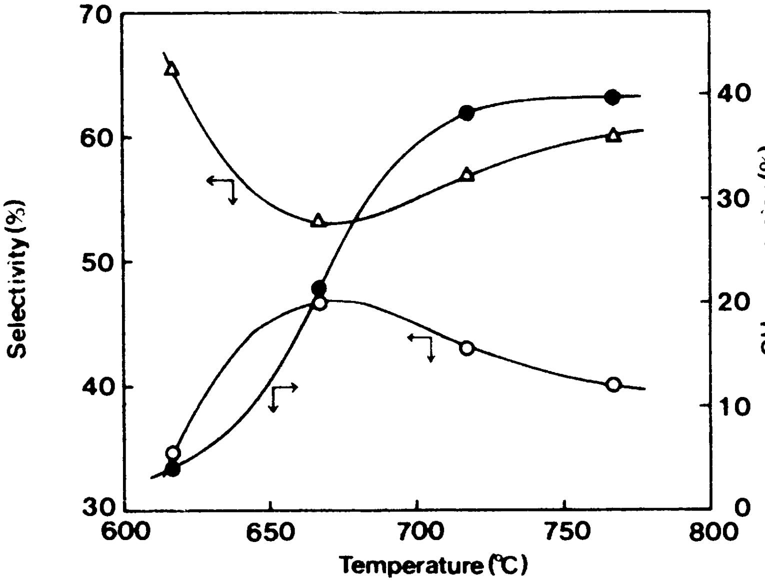

Figure 1 *Effect of reaction temperature on the partial oxidation of methane over* Li/MgO: ○ *selectivity to* C_2 *compounds;* △ *selectivity to* CO *and* CO_2*;* ● CH_4 *conversion* (Reproduced by permission from *Nature*, 1985, **314**, 721)

temperature reaction are: C_2H_6, C_2H_4, CO, CO_2, H_2, H_2O and to a lesser extent higher hydrocarbons (C_3 hydrocarbons are typically found at an order of magnitude lower than the C_2 hydrocarbons). Oxygenated products, *e.g.* CH_3OH and CH_2O are found in only trace amounts, which is in contrast to earlier gas phase studies.[5,15]

Based on these early studies two catalysts are now being evaluated at pilot plant scale. Sofranko *et al.*[16,17] have described a cyclically fed process based on a supported manganese oxide catalyst. Under conditions of cyclic feeding they have shown that selectivity and conversion are related by a '100% rule' (methane conversion and C_2 selectivity roughly sum to 100%, see Figure 2). Co-feeding of methane and oxygen results in a loss of at least 10% in C_2 selectivity. It is apparent that methane conversion decreases significantly in only a short reaction time, and hence rapid cycling between methane and oxygen is required for this process to be viable. Edwards and Tyler[18,19] have described a co-feeding process based on lithium-promoted magnesium oxide operated in a fluidized bed reactor,

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[15] E. H. Boomer and V. Thomas, *Can. J. Res., Sect. B*, 1937, **15**, 401.

[16] C. A. Jones, J. J. Leonard, and J. A. Sofranko, *J. Catal.*, 1987, **103**, 311.

[17] J. A. Sofranko, J. J. Leonard, C. A. Jones, A. M. Gaffney, and H. P. Withers, *Catal. Today*, 1988, **3**, 127.

[18] J. H. Edwards and R. J. Tyler, *Stud. Surf. Sci. Catal.*, 1988, **36**, 395.

[19] J. H. Edwards and R. J. Tyler, in Proceedings 1st Workshop on Catalytic Methane Conversion, Bochum 1988, *Catal. Today*, 1989, **4**, 345.

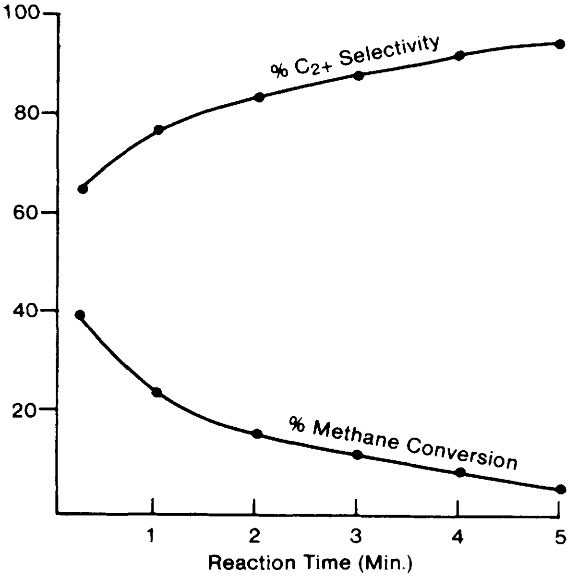

Figure 2 *Methane oxidation in the absence of co-fed oxygen at* 850 °C *and* 860 ml CH_4/ml cat./h over 15% Mn, 5% $Na_4P_2O_2/SiO_2$
(Reproduced by permission from *J. Catal.*, 1987, **103**, 311)

which can also give C_2 selectivities in excess of 80%, at low conversions (Figure 3), and so it is clear that cyclic feed operation is not necessary for the attainment of high product selectivity. An important question remains concerning the comparison of methane oxidation using cyclic and co-feed experimental regimes; it has to be considered whether the methane activation process is the same for the two processes. Recent results[20] have shown that, in the absence of gas phase oxygen, lattice oxygen in MgO or Li/MgO is inactive for methane oxidation, *i.e.* the stoicheiometric reaction is not observed, and hence methane oxidation in the co-fed regime must involve reaction with an adsorbed oxygen species. With supported manganese oxide the stoicheiometric oxidation is observed implicating the involvement of lattice oxide ions O^{2} , possibly at low co-ordinate defect sites as found for ammoxidation catalysts,[21] as active centres. Hence, superficially it could be concluded that the methane activation step could be different for the two experimental regimes. However, in the presence of gas phase oxygen an adsorbed oxygen species could also become important for the manganese oxide catalysts, and consequently further experimental work is required to address this question fully.

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[20] G. J. Hutchings, M. S. Scurrell, and J. R. Woodhouse, *J. Chem. Soc., Faraday Trans. 1*, in press.
[21] K. Aykam, O. Halvorson, A. W. Sleight, and D. B. Rodgers, *J. Catal.*, 1975, **35**, 401.

Table 1 *Methane oxidation with molecular oxygen using group IIA metal oxide catalysts*

Catalyst	CH_4/O_2 *mole ratio*	*GHSV* h^{-1}	*T* °C	*Conversion %* CH_4	O_2	*C_2 hydrocarbon* *Selectivity %*	*Yield %*	*ethane*/*ethene*	*Ref.*
7% Li/MgO	1.6	2 990	720	42.8	—	45.4	19.4	0.57	*a,b*
7% Li/MgO	2.0	2 990	720	37.8	—	50.3	19.0	0.62	*a,b*
7% Li/MgO	3.1	2 990	720	29.1	—	58.1	16.9	0.66	*a,b*
BeO	9.3	31.1*	740—750	9	99	22	2.0	—	*c*
MgO	9.3	0.2*	740—750	12	93	47	5.6	—	*c*
CaO	9.3	0.1*	740—750	11	94	55	6.1	—	*c*
SrO	9.3	23.1*	740—750	8	88	72	5.8	—	*c*
BaO	9.3	14.5*	740—750	14	98	70	9.8	—	*c*
3% Li/CaO	9.3	0.4*	740—750	14	97	72	10.1	—	*c*
3% Na/CaO	9.3	0.3*	740—750	16	95	76	12.2	—	*c*
3% K/CaO	9.3	0.4*	740—750	14	83	72	10.1	—	*c*
MgO	200	12*	800	—	—	—	0.1	0.56	*d*
20% Bi/MgO	100	12*	800	—	—	—	0.3	3.00	*d*
15% K/MgO	100	12*	800	—	—	—	2.3	0.61	*d*
MgO	3.5	667	550	3.0	—	0	0	—	*e,f,g,h*
MgO	3.5	667	720	5.2	100	58.1	3.0	1.83	*e,f,g,h*
5% Li/MgO	3.3	648	550	2.0	—	22.5	0.45	3.50	*e,f,g,h*
5% Li/MgO	3.3	648	720	2.7	37.0	65.4	1.76	1.47	*e,f,g,h*
3% Li/BeO	3.0	0.61*	640	19.8	69.6	51.0	10.1	—	*i*
3% Li/BeO	3.0	0.61*	680	27.5	96.6	52.0	14.3	—	*i*
3% Li/BeO	3.0	0.061*	760	28.4	93.3	58.5	16.6	—	*i*
MgO	20	0.75*	750	11.3	—	39.1	4.4	3.76	*j*
5—10% Li/MgO	20	0.75*	750	7.5	—	76.6	5.7	2.73	*j*

[a] Ref. 13. [b] Ref. 38. [c] Ref. 28. [d] K. I. Aika and T. Nishiyama, *Proc. 9th Int. Congr. Catal., Calgary*, ed. M. J. Phillips and M. Ternan, Chemical Institute of Canada, 1988, **2**, 907. [e] Ref. 64. [f] Ref. 35. [g] Ref. 25. [h] Ref. 36. [i] T. Doi, Y. Utsumi, and I. Matsuura, *Proc. 9th Int. Congr. Catal., Calgary*, ed. M. J. Phillips and M. Ternan, Chemical Institute of Canada, 1988, **2**, 937. [j] R. Burch, G. D. Squire, and S. C. Tsang, *Appl. Catal.*, 1988, **43**, 105. * denotes W/F g s ml^{-1}

Table 2 *Methane oxidation with molecular oxygen using lanthanide metal oxide catalysts*

Catalyst	CH_4/O_2 *mole ratio*	*GHSV* h^{-1}	*T* °C	*Conversion %* CH_4	O_2	*C_2 hydrocarbon* *Selectivity %*	*Yield %*	*ethane*/*ethene*	*Ref.*
La_2O_3	4.6	1.0*	650	10	74	8	0.8	1.7	*a,b*
CeO_2	4.6	1.0*	650	9	100	3	0.3	0.0	*a,b*
Pr_6O_{11}	4.6	1.0*	650	11	100	20	2.2	2.3	*a,b*
Nd_2O_3	4.6	1.0*	650	14	99	37	5.2	3.0	*a,b*
Sm_2O_3	4.6	1.0*	650	15	96	37	5.6	2.4	*a,b*
Dy_2O_3	4.6	1.0*	650	13	91	24	3.1	2.7	*a,b*
La_2O_3	10.0	0.22*	740	18.8	—	40	7.5	—	*c*
Sm_2O_3	10.0	0.22*	780	12.2	—	54	6.6	—	*c*
Gd_2O_3	10.0	0.22*	770	12.1	—	48	5.8	—	*c*
Tb_4O_7	10.0	0.22*	820	7.8	—	28	2.2	—	*c*
Dy_2O_3	10.0	0.22*	793	12.9	—	53	6.8	—	*c*
La_2O_3	37.0	2.4*	725	3.6	88	71.0	2.5	1.5	*d*
La_2O_3	8.8	2.4*	725	9.4	91	46.6	4.4	1.0	*d*
La_2O_3	3.4	2.4*	725	19.7	93	23.7	4.7	0.8	*d*
La_2O_3	3.0	900	710	22.7	100	15.8	3.6	2.2	*e*
5% Li/La_2O_3	3.3	700	710	10.3	33	49.9	5.1	2.2	*e*
Sm_2O_3	3.1	592	710	19.1	100	15.3	2.9	14.3	*e*
5% Li/Sm_2O_3	3.0	857	710	24.5	87	52.9	13.0	0.9	*e*

La_2O_3	6.0	37 500	750	19.6	100	56.6	11.1	1.2	f
1% Li/La_2O_3	6.0	37 500	800	21.6	100	70.2	15.2	1.2	f
1% Na/La_2O_3	6.0	37 500	800	20.0	100	64.6	12.9	1.1	f
1% K/La_2O_3	6.0	37 500	800	20.6	100	60.4	12.4	1.0	f
1% Sr/La_2O_3	6.0	37 500	750	20.9	100	63.6	13.3	1.2	f,g
Sm_2O_3	6.0	37 500	750	12.9	100	53.0	9.5	1.3	f
Sm_2O_3	20.0	0.75*	750	13.3	—	52.3	7.0	2.4	h
5–10% Li/Sm_2O_3	20.0	0.75*	750	9.3	—	64.0	6.0	1.5	h
Sm_2O_3	2.5	0.6*	750	29.0	100	40.0	11.6	—	i
10% Li/Sm_2O_3	2.5	0.6*	750	37.0	100	57.0	21.1	—	i
10% Na/Sm_2O_3	2.5	0.6*	750	37.0	100	50.0	18.5	—	i
10% K/Sm_2O_3	2.5	0.6*	750	37.0	100	52.0	19.2	—	i
10% Rb/Sm_2O_3	2.5	0.6*	750	37.0	100	46.0	17.0	—	i
10% Cs/Sm_2O_3	2.5	0.6*	750	37.0	100	45.0	16.6	—	i
CeO_2	2.0	0.56*	750	—	—	0	0	—	f
20% Li/CeO_2	2.0	0.56*	750	28.6	—	50.0	14.3	—	f
20% Na/CeO_2	2.0	0.56*	750	33.4	—	41.0	13.7	—	f
20% K/CeO_2	2.0	0.56*	750	56.5	—	23.0	13.0	—	f

[a] K. Otsuka, K. Jinno, and A. Morikawa, *Chem. Lett.*, 1985, 499. [b] K. Otsuka and T. Nakajima, *Inorg. Chim. Acta*, 1986, **120**, L27. [c] Ref. 68. [d] Ref. 52. [e] Ref. 35. [f] J. M. DeBoy and R. F. Hicks, *J. Chem. Soc., Chem. Commun.*, 1988, 982. [g] J. M. DeBoy and R. F. Hicks, *J. Catal.*, 1988, **113**, 517. [h] R. Burch, G. D. Squire, and S. C. Tsang, *Appl. Catal.*, 1988, **43**, 105. [i] K. Otsuka, Q. Liu, M. Hatano, and A. Morikawa, *Chem. Lett.*, 1987, 1835. * denotes W/F g s ml^{-1}

Table 3 *Methane oxidation with molecular oxygen using transition metal oxides*

Catalyst	CH_4/O_2 *mole ratio*	*GHSV* h^{-1}	*T* °C	*Conversion* %		C_2 *hydrocarbon*		$\frac{ethane}{ethene}$	*Ref.*
				CH_4	O_2	*Selectivity* %	*Yield* %		
MnO_2/α-Al_2O_3	†	96	800	11	—	45	5	—	*a*
CdO/α-Al_2O_3	†	96	800	10	—	40	4	—	*a*
TiO_2/α-Al_2O_3	†	96	800	1.7	—	<6	0.1	—	*a*
α-Al_2O_3	†	96	800	1.8	—	11	0.2	—	*a*
1% Li/TiO_2	2	0.42*	800	16.7	42	75	12.5	1.2	*b*
15% MnO_2/SiO_2	†	600	800	30.0	—	50	15.0	0.38	*c*
15% MnO_2/SiO_2	†	860	850	22.0	—	61	13.4	0.30	*d*
15% MnO_2/SiO_2	5	4 800	900	22.0		59	13.0	0.51	*d*
$NaCl/MnO_2$	2	0.23*	750	32.0	98	49	15.7	0.17	*e*
10% MnO_2/SiO_2	3.3	1 000	750	20.6	—	30.6	6.3	0.76	*f*
MnO_2	20	0.75*	750	6	—	8.9	0.5	0	*g*
15% MnO_2/SiO_2	20	0.75*	750	6	—	16.8	1.0	5.0	*g*
$NaCl/15\%\ MnO_2/SiO_2$	20	0.75*	750	7	—	36.5	2.6	4.1	*g*

NiO	2.0	0.6*	750	29.9	81	0	0	—	*h*
LiCl/NiO	2.0	0.6*	750	25.9	57	71.8	18.6	0.27	*h*
Li_2CO_3/NiO	2.0	0.6*	750	25.9	70	48.9	12.7	0.85	*h*
$LiNO_3$/NiO	2.0	0.6*	750	26.1	75	55.8	14.6	1.34	*h*
NaCl/NiO	2.0	0.6*	750	17.9	44	34.7	6.2	7.20	*h*
12% Li/ZnO	2	0.167*	680	16.7	42.5	56.2	9.4	—	*i*
12% Li/ZnO	2	0.167*	720	30.6	81.6	60.5	18.5	—	*i*
12% Li/ZnO	2	0.167*	760	34.6	89.9	59.5	20.6	—	*i*
0.18% Li/ZnO	2	4.8*	650	5.1	11.7	51.1	2.6	3.91	*j*
0.18% Li/ZnO	2	4.8*	700	13.9	25.3	59.0	8.2	1.15	*j*
0.18% Li/ZnO	2	4.8*	720	21.4	32.4	52.6	11.3	1.15	*j*
0.18% Li/ZnO	2	4.8*	750	28.2	55.5	53.3	15.0	0.85	*j*

[a] Ref. 9. [b] G. S. Lane and E. Wolf, *Proc. 9th Int. Cong. Catal., Calgary*, ed. M. J. Phillips and M. Ternan, Chemical Institute of Canada, 1988, **2**, 944. [c] Ref. 16. [d] Ref. 17. [e] K. Otsuka and T. Komatsu, *J. Chem. Soc., Chem. Commun.*, 1987, 338. [f] Kh. M. Minachev, N. Ya. Usachev, Yu. S. Khodakov, L. I.. Kozlov, V. N. Udut, and O. A. Fomin, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1987, 504. [g] R. Burch, G. D. Squire, and S. C. Tsang, *Appl. Catal.*, 1988, **43**, 105. [h] K. Otsuka, Q. Liu, M. Hatano, and A. Morikawa, *Inorg. Chim. Acta*, 1986, **118**, L24. [i] I. Matsuura, Y. Utsumi, M. Nakai, and T. Doi, *Chem. Lett.*, 1986, 1981. [j] Ref. 70. * denotes W/F g s ml^{-1}. † cyclic operation, no co-fed oxidant

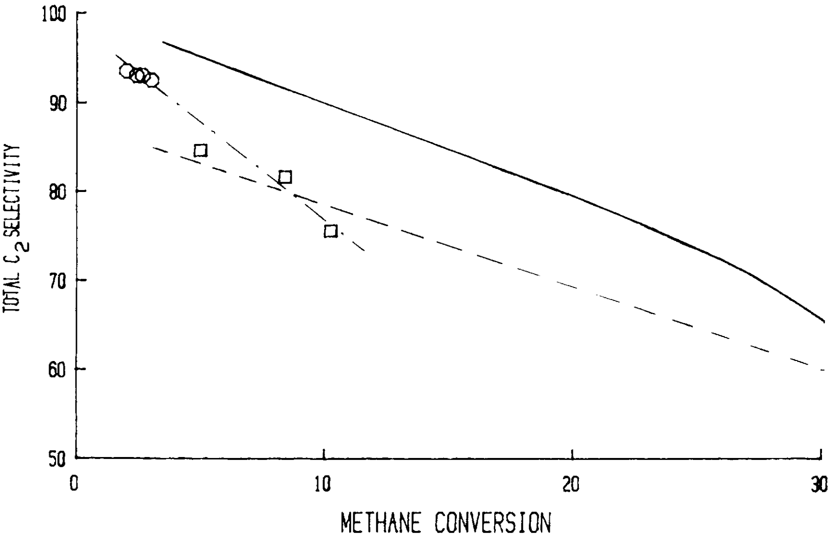

Figure 3 *Comparison of* C_2 *selectivity for co-fed and cyclic oxidation of methane:* (i) *co-fed* CH_4/O_2 *oxidation over* Li/MgO, ○ 1.1% O_2 *and* 90% CH_4, □ 9.4% O_2 *and* 90% CH_4, *data taken from ref.* 18; (ii) CH_4 *oxidation over* 15% Mn, 5% $Na_4P_2O_2/SiO_2$, —— *cyclic operation*, – – – – *co-fed* CH_4/O_2, *data taken from ref.* 16.

It could be concluded from these early studies that the selectivity to C_2 hydrocarbons for any particular catalyst is related to the concentration of gas phase oxygen co-fed with the methane (*e.g.* see Figure 3). This is not surprising since the initial products resulting from the activation of methane will be considerably more reactive with respect to oxygen and hence excess oxygen will result in consecutive oxidation of the initial products.

Since the early studies of Keller and Bhasin and Lunsford a large scale catalyst screening and evaluation exercise has been carried out by a large number of workers. As a result, the majority of the simple metal oxides have been examined as catalysts for the partial oxidation of methane. Representative data from these studies are summarized in Tables 1—5 for different classification of metal oxides. A striking feature of these studies is that the product distribution remains invariant to a greater extent (*i.e.* C_2H_6, C_2H_4, CO, CO_2, H_2, H_2O and lesser amounts of C_{3+} hydrocarbons) and CH_3OH, CH_2O or other oxygenates have been reported for only a very small range of catalyst formulations.[22–24] It is possible that at the elevated temperature, >600 °C, required to observe

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[22] K. Otsuka, T. Komatsu, K. Jinno, Y. Uragami, and A. Morikawa, *Proc. 9th Int. Cong. Catal.*, Calgary, ed. M. J. Phillips and M. Ternan, Chemical Institute of Canada, 1988, **2**, 905.

[23] E. Mac Giolla Coda, E. Mulhall, Rivan Hoek, and B. K. Hodnett, in Proceedings 1st Workshop on Catalytic Methane Conversion, Bochum 1988, *Catal. Today*, 1989, **4**, 383.

[24] S. Kasztelan and J. B. Moffat, *J. Chem. Soc., Chem. Commun.*, 1987, 1663.

Table 4 *Methane oxidation with molecular oxygen using group IIIA, IVA, and VA metal oxide catalysts*

Catalyst	CH_4/O_2 *mole ratio*	*GHSV* h^{-1}	*T* °C	*Conversion %*		C_2 *hydrocarbon*		$\frac{ethane}{ethene}$	*Ref.*
				CH_4	O_2	*Selectivity %*	*Yield %*		
$Tl_2O_3/\alpha\text{-}Al_2O_3$	†	96	800	6.8	—	44	3.0	—	*a*
$SnO_2/\alpha\text{-}Al_2O_3$	†	96	800	8.4	—	4.8	0.4	—	*a*
$PbO/\alpha\text{-}Al_2O_3$	†	96	800	4.4	—	43	2.0	—	*a*
$Bi_2O_3/\alpha\text{-}Al_2O_3$	†	96	800	4.4	—	9.1	0.4	—	*a*
5% SnO_2/SiO_2	†	600	700	3.2		20.9	0.7	1.90	*b*
5% SnO_2/SiO_2	†	600	800	10.1	—	29.3	3.0	0.86	*b*
5% Sb_2O_3/SiO_2	†	600	700	1.2	—	11.8	0.1	1.11	*c*
5% Sb_2O_3/SiO_2	†	600	800	2.7	—	21.0	0.6	1.13	*c*
24% $PbO/\alpha\text{-}Al_2O_3$	5	29 800	751	14.2	—	38.2	5.4	—	*d*
6.5% PbO/Al_2O_3	10	0.11*	740	—	99	12.8	—	2.88	*e,f*
36% PbO/Al_2O_3	10	0.22*	740	—	95.1	56.2	—	2.2	*e,f*
7% Bi_2O_3/Al_2O_3	10	0.011*	640	6.6	87	23.9	1.6	—	*g*
7% PbO/Al_2O_3	10	0.011*	640	4.2	63	7.6	0.3	—	*g*
7% SnO_2/Al_2O_3	10	0.011*	640	6.4	85	14.7	0.9	—	*g*
PbO	100	2*	750	—	—	—	0.1	—	*h*
$Bi_2O_3/P_2O_5/K_2O/MgO$	8	—	710	12.9	100	59	7.6	—	*i*

[a] Ref. 9. [b] C. A. Jones, J. J. Leonard, and J. A. Sofranko, *US Patent*, 4444984 (1984). [c] C. A. Jones, J. J. Leonard, and J. A. Sofranko, *US Patent*, 4443664 (1984). [d] Ref. 17. [e] Ref. 12. [f] W. Bytyn and H. Baerns, *Appl. Catal.*, 1986, **28**, 199. [g] I. T. A. Emesh and Y. Amenomiya, *J. Phys. Chem.*, 1986, **90**, 4785. [h] K.-I. Aika and T. Nishiyama, *J. Chem. Soc., Chem. Commun.*, 1988, 70. [i] G. W. Keulks and M. Yu, *React. Kinet. Catal. Lett.*, 1987, **35**, 361. * denotes W/F g s ml^{-1}. † denotes cyclic operation, methane and oxidant fed separately

Table 5 *Methane oxidation with molecular oxygen using complex oxide catalysts*

Catalyst	CH_4/O_2 *mole ratio*	*GHSV* h^{-1}	*T* °C	*Conversion %*		*C₂ hydrocarbon*		*ethane*/*ethene*	*Ref.*
				CH_4	O_2	*Selectivity %*	*Yield %*		
$LaAlO_3$	5.0	2 000	710	25.3	94.7	48.4	12.2	—	*a,b,c*
$PbMoO_4$	8.3	33.6	740	1	3	19	0.2	—	*d,e*
$PbWO_4$	8.3	55.3	740	8	100	5	0.4	—	*d.e*
$PbCrO_4$	8.3	16.1	740	10	100	4	0.4	—	*d,e*
$Pb_3(PO_4)_2$	8.3	13.6	740	9	87	51	0.5	—	*d,e*
$PbSO_4$	8.3	52.4	740	8	63	63	0.5	—	*d.e*
$Bi_2Sn_2O_7$	4.8	0.22*	508	13	—	25	3.3	—	*f*
$SrCeO_3$	2.0	0.72*	750	44.2	—	49.3	21.8	1.18	*g*
$SrCe_{0.9}Yb_{0.1}O_{2.95}$	2.0	0.72*	750	52.6	—	60.1	31.6	0.66	*g*
$Ce_{0.95}Yb_{0.1}O_{1.95}$	2.0	0.72*	750	25.1	—	2.9	0.7	0.0	*g*
CeO_2	2.0	0.72*	750	31.5	—	12.7	4.0	0.11	*g*
SrO	2.0	0.72*	750	25.3	—	62.4	15.8	0.37	*g*
Yb_2O_3	2.0	0.72*	750	28.3	—	44.5	12.6	0.98	*g*
$AgCrO_2$	6	1 500	697	10.5	99.0	8.4	0.9	0.0	*h*
$NaFeO_2$	6	1 500	697	9.1	99.2	9.1	0.8	8.0	*h*
$LiNiO_2$	6	1 500	697	25.9	46.6	46.7	12.1	1.5	*h*

$LiFeO_2$	6	1 500	697	8.5	99.1	9.1	0.8	4.7	*h*
$LiYO_2$	6	1 500	697	22.0	100	58.2	12.8	1.1	*h*
Na_2CeO_3	6	1 500	697	16.7	99.8	43.2	7.2	4.3	*h*
$LiTiO_3$	6	1 500	697	11.5	98.0	16.2	1.9	12.5	*h*
Y_2O_3	6	1 500	697	10.0	100	37.2	3.7	1.5	*h*
$Pb_2Mn_2Si_2O_9/SiO_2$	7.7	1 300	650	4.4	—	42.2	1.9	—	*i*
$Pb_2Mn_2Si_2O_9/SiO_2$	7.7	1 300	700	9.4	—	61.9	5.8	—	*i*
$Pb_2Mn_2Si_2O_9/SiO_2$	7.7	1 300	750	17.5	—	63.9	11.2	—	*i*
$Pb_2Mn_2Si_2O_9/SiO_2$	7.7	1 300	800	30.0		67.5	20.3	—	*i*
$LiBi_3O_4Cl_2$	2.0	82.8*	750	22.1	—	77.1	17.0	0.29	*j,k*
$NaBi_3O_4Cl_2$	2.0	82.8*	750	22.6	—	83.1	18.3	0.29	*j,k*
$KBi_3O_4Cl_2$	2.0	82.8*	750	23.8	—	82.3	19.6	0.26	*j,k*
$AgBi_3O_4Cl_2$	2.0	82.8*	750	23.7	—	65.0	15.4	0.20	*j,k*
$PbBiO_2Cl$	2.0	82.8*	750	13.7		72.9	10.0	0.56	*j,k*
$BiOCl$	2.0	82.8*	750	23.0	—	71.1	16.4	0.23	*j,k*
Bi_2O_3	2.0	82.8*	750	9.1	—	31.1	2.8	3.33	*j,k*

[a] H. Imai and T. Tagawa, *J. Chem. Soc., Chem. Commun.*, 1986, 52. [b] H. Imai, T. Tagawa, and N. Kamide, *J. Catal.*, 1987, **106**, 394. [c] H. Imai, T. Tagawa, N. Kamide, and S. Wada, *Proc. 9th Int. Cong. Catal., Calgary*, ed. M. J. Phillips and M. Ternan, Chemical Institute of Canada, 1988, **2**, 952. [d] J. A. S. P. Carreiro and M. Baerns, *React. Kinet. Catal. Lett.*, 1987, **35**, 349. [e] Ref. 28. [f] Ref. 71. [g] Ref. 30. [h] R. K. Unger, X. Zhang, and R. M. Lambert, *Appl. Catal.*, 1988, **42**, L1. [i] J. M. Thomas, X. Zhang, and J. Stachurski, *J. Chem. Soc., Chem. Commun.*, 1988, 162. [j] W. Ueda and J. M. Thomas, *Proc. 9th Int. Congr. Catal., Calgary*, ed. M. J. Phillips and M. Ternan, Chemical Institute of Canada, 1988, **2**, 960. [k] W. Ueda and J. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 1988, 1148. * denotes W/F g s ml^{-1}

Table 6 *Specific activity data for methane oxidation with molecular oxygen using oxide catalysts*

Catalyst	CH_4/O_2 *mole ratio*	*T* °C	*Methane feed-rate* mol gcat^{-1} h^{-1}	10^4 *Specific Activity/mol product* m^{-2} h^{-1}							*Ref.*
				H_2	CO_2	CO	C_2H_4	C_2H_6	*Total* C_2	*Total C*†	
5% Li/MgO	3	710	0.0616*	7.7	16.1	1.3	2.5	8.0	10.5	38.4	*a*
MgO	3	710	0.0616*	3.7	4.5	1.3	0.8	0.8	1.6	9.0	*a*
5% Li/La_2O_3	3	710	0.0616*	20	24	5.1	1.8	8.9	10.7	50.5	*a*
La_2O_3	3	710	0.0616*	11	17	1.8	4.2	4.9	9.1	37.0	*a*
5% Li/Sm_2O_3	3	710	0.0616*	16	97	3.9	29.0	42.0	71.0	242.9	*a*
Sm_2O_3	3	710	0.0616*	19	28	3.5	5.0	6.8	11.8	55.1	*a*
MgO	2.1	700	0.0148	—	—	—	0.02	0.06	0.08	1.4	*b*
7% Li/MgO	2.1	700	0.0185	—	—	—	3.0	3.0	6.0	16.5	*b*
20% Na/MgO	2.1	700	0.0185	—	—	—	0.21	0.43	0.64	4.2	*b*
30% K/MgO	2.1	700	0.0185	—	—	—	0	0.02	0.02	3.0	*b*
CaO	2.1	700	0.0185	—	—	—	0.05	0.54	0.59	7.9	*b*
5% Li/CaO	2.1	700	0.0185	—	—	—	2.8	3.9	6.7	16.7	*b*
15% Na/CaO	2.1	700	0.0185	—	—	—	4.9	5.5	10.4	30.8	*b*
23% K/CaO	2.1	700	0.0185	—	—	—	3.5	4.9	8.4	28.7	*b*

Y_2O_3	46	700	0.0122		—	—	0.20	0.46	0.66	1.7	*c*
La_2O_3	46	700	0.0122	—	—	—	0.15	0.28	0.43	1.0	*c*
Sm_2O_3	46	700	0.0122	—	—	—	1.1	2.3	3.4	7.3	*c*
Gd_2O_3	46	700	0.0122		—	—	0.37	0.83	1.2	3.0	*c*
Ho_2O_3	46	700	0.0122	—	—	—	0.24	1.16	1.4	3.3	*c*
Yb_2O_3	46	700	0.0122	—	—	—	0.1	0.5	0.6	11.4	*c*
PbO	46	700	0.0122	—	—	—	0.2	2.3	2.5	—	*c*
Bi_2O_3	46	700	0.0122	—	—	—	0.3	1.6	1.9	5.1	*c*
$LaAlO_3$	1	710	0.179*	—	—	—	—	—	43.1	178	*d*
La_2O_3	1	710	0.179*	—	—	—	—	—	8.7	37.8	*d*
Sm_2O_3	1	710	0.179*	—	—	—	—	—	22.5	120	*d*
CeO_2	2	750	0.0298	—	—	—	1.5	0.2	1.7	26.8	*e*
Yb_2O_3	2	750	0.0298	—	—	—	2.2	2.2	4.4	19.7	*e*
$Ce_{0.95}Yb_{0.1}O_{1.95}$	2	750	0.0298	—	—	—	0	0.2	0.2	83.4	*e*
SrO	2	750	0.0298	—	—	—	5.6	2.0	7.6	24.4	*e*
$SrCeO_3$	2	750	0.0298	—	—	—	12.5	14.7	27.2	110.0	*e*
$SrCe_{0.9}Yb_{0.1}O_{2.95}$	2	750	0.0298	—	—	—	20.2	13.4	33.6	112.0	*e*

[a] Ref. 20. [b] C. H. Lin, T. Ho, J.-X. Wang, and J. H. Lunsford, *J. Am. Chem. Soc.*, 1987, **109**, 4808. [c] Ref. 58. [d] H. Imai and T. Tagawa, *J. Chem. Soc., Chem. Commun.*, 1986, 525. [e] Ref. 30. * methane feed-rate mol mlcat^{-1} h^{-1}. † based on methane converted into carbon-containing products

formation of C_2 hydrocarbons, the oxygenated products, such as CH_3OH and CH_2O, are unstable and decompose possibly to carbon oxides and hydrogen. However, formation of oxygenates at lower temperatures is not reported, and in studies where low temperature investigations have been made[25] no enhanced level of oxygenated products is observed. While the product type remains invariant, product selectivity is markedly affected by the choice of metal oxide as catalyst, but even for the most selective oxides the C_2 yield rarely exceeds 25%, an observation consistent with the 100% rule previously noted by Sofranko *et al.*[17] It is also apparent that the ethene/ethane product ratio varies markedly for all these studies. However, as has been recently noted by van Kasteren *et al.*,[26] this may be caused by the design of the reactor, particularly the volume of the heated zone downstream of the catalyst bed, and for most published studies summarized in this review precise details of the reactor are not given. Another general feature from these studies is that catalyst activity is related to basicity[27,28] and the increase in catalyst basicity increases activity. This is most readily observed from the addition of alkali metal additives to single oxides such as MgO and CaO (Table 1) which results in catalysts that are significantly more selective for C_2 production. The role of alkali promoters will be considered in Section 3A.

The main observation that can be made from the summary of the catalytic studies (Tables 1—5) is that a very wide range of experimental conditions have been used. For example, studies have used CH_4/O_2 mole ratios from 2:1 to 200:1 and in some studies additional inert diluent is utilized. In view of the diversity of the experimental work it is extremely difficult to draw any broad conclusions from these studies concerning catalyst selectivity. It is apparent that metal oxides exhibit a range of catalytic activities but to some extent these variations are due solely to the intrinsic surface area, and hence density of surface sites, of the oxide. The importance of surface area with respect to the yield of C_2 hydrocarbons has been noted by Aika[29] and it was concluded that low surface area materials were preferable, this being one of the major reasons for the large scale use of alkali metal compound additives since this results in loss of surface area due to sintering. It is therefore important to compare different catalysts in terms of their specific activity (moles product $m^{-2}\,h^{-1}$) and these data are summarized for the most active catalysts in Table 6. On this basis it is now possible to compare the relative activities of these oxides. At 700—710 °C catalysts can be ranked in order of decreasing specific activity for C_2 production as follows:

$$Li/Sm_2O_3 > Na/CaO > K/CaO > LaAlO_3 > Sm_2O_3 \sim Li/CaO > PbO > Bi_2O_3 > Ho_2O_3 > Gd_2O_3 > Li/MgO \sim Li/CaO \sim Yb_2O_3 \sim Y_2O_3 > Na/MgO \sim CaO > MgO.$$

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[25] G. J. Hutchings, M. S. Scurrell, and J. R. Woodhouse, *Stud. Surf. Sci. Catal.*, 1988, **36**, 415.

[26] H. M. N. van Kasteren, J. W. M. H. Geerts, and K. van der Wiele, ref. 22, p. 930.

[27] K.-I. Aika and T. Nishiyama, in Proceedings 1st Workshop on Catalytic Methane Conversion, Bochum 1988, *Catal. Today*, 1989, **4**, 271.

[28] J. A. S. P. Carreiro, G. Follmer, L. Lehmann, and M. Baerns, ref. 22, p. 891.

[29] E. Iwamatsu, T. Mosiyama, N. Takasaki, and K. Aika, *Stud. Surf. Sci. Catal.*, 1988, **36**, 373.

At the higher temperature of 750 °C a recent study by Machida and Enyo[30] indicates that $SrCeO_3$ may exhibit a higher specific activity than Li/Sm_2O_3. For this summary it may be concluded that, although catalyst selectivities may be similar, there exists a very wide range of specific activities spanning almost two orders of magnitude. Considerable scope exists to further improve on these specific activities, and as yet no detailed study has been published concerning optimization of the specific activity by using improved methods of catalyst preparation.

B. Nitrous Oxide as Oxidant.—A number of studies have specifically utilized nitrous oxide as oxidant because of the specific selectivity effect that can be achieved. Liu *et al.*[31] and Zhen *et al.*[32] noted that with Mo and V catalysts methane was oxidized to methanol with N_2O as oxidant. Subsequently, Solymosi *et al.*[33] demonstrated that for Bi_2O_3 as catalyst use of N_2O resulted in the formation of high selectivities for formaldehyde at 550 °C, a temperature at which O_2 is inactive. Addition of SnO_2 significantly enhanced this effect and it was considered that one role of the SnO_2 was to facilitate the decomposition of N_2O enabling it to participate directly in the oxidation process. However, a number of other studies for Sm_2O_3,[34,35] MgO,[36] and Li/MgO[36] have shown that use of N_2O does not significantly enhance the production of oxygenates for these catalysts, and hence this is not a general feature of this oxidant. Indeed, a recent study by Kasztelan and Moffat[24] demonstrated that when O_2 was used as oxidant with silica as catalyst significant yields of formaldehyde were observed, in contrast to the results with N_2O where complete oxidation was observed.

Few comparative studies of the use of N_2O and O_2 as oxidants have been reported, and these are summarized in Table 7. The main conclusion from these studies is that under comparable reaction conditions, with N_2O as oxidant, significantly lower methane conversions are observed with increased C_2 selectivity, particularly to ethane. The increase in selectivity to ethane is most marked at lower reaction temperatures. The marked increase in C_2 selectivity may just be a result of the selectivity/conversion relationships that exist for these catalysts, *i.e.* higher C_2 selectivities are generally observed at lower methane conversions (*e.g.* see Figure 3). However, recent evidence[20] has shown this not to be the case, and at comparable conversions N_2O is always more selective for C_2 formation than O_2 as oxidant (Figure 4). The decreased oxidation activity observed with N_2O is probably due to two factors. First, on a molar basis N_2O can be considered to have only half the potential for stoicheiometric reaction compared to O_2, but experiments where this has been taken into account have shown that N_2O is much less active than O_2.[34] Second, the decomposition of N_2O to an active

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[30] K. I. Machida and M. Enyo *J. Chem. Soc., Chem. Commun.*, 1987, 1639.

[31] H. F. Liu, R. S. Liu, K. Y. Liew, R. W. Johnson, and J. H. Lunsford, *J. Am. Chem. Soc.*, 1984, **106**, 4117.

[32] K. J. Zhen, M. M. Khan, C. H. Mak, K. B. Lewis, and G. A. Somorjai, *J. Catal.*, 1985, **94**, 501.

[33] F. Solymosi, I. Tombacz, and G. Katson, *J. Chem. Soc., Chem. Commun.*, 1985, 1455.

[34] K. Otsuka and K. Nakajima, *J. Chem. Soc., Faraday Trans.*, 1987, **83**, 1315.

[35] G. J. Hutchings, M. S. Scurrell, and J. R. Woodhouse, in Proceedings 1st Workshop on Catalytic Methane Conversion, Bochum 1988, *Catal. Today*, 1989, **4**, 371.

[36] G. J. Hutchings, M. S. Scurrell, and J. R. Woodhouse, *J. Chem. Soc., Chem. Commun.*, 1987, 1388.

Table 7 *Comparison of nitrous oxide and molecular oxygen as oxidants for methane*

Catalyst	*Oxidant*	CH_4/*oxidant* *mole ratio*	*T* °C	*GHSV* h^{-1}	*Conversion mole %* CH_4	*Oxidant*	*Product Selectivity*[a] *mole %* CO_2	CO	C_2H_4	C_2H_6	*Total* C_2	*Ref.*
MgO	O_2	3.5	550	667	3.0	—	66.2	31.8	0.4	1.6	2.0	*b,c*
	N_2O	3.3	550	563	1.8	—	96.1	2.0	0.3	1.6	1.9	*b,c*
	O_2	3.5	710	667	5.2	100	50.0	3.2	28.4	18.4	46.8	*b,c*
	N_2O	3.3	710	545	3.0	98	88.9	6.8	2.7	1.6	4.3	*b,c*
Li/MgO	O_2	3.3	550	648	2.0	—	59.8	17.7	5.0	17.5	22.5	*b,c*
	N_2O	3.4	550	638	0.2	—	17.2	0	7.0	75.8	82.8	*b,c*
	O_2	3.3	710	648	2.7	37	33.0	1.6	26.5	38.9	65.4	*b,c*
	N_2O	3.4	710	638	0.3	2.8	51.9	0	9.3	38.9	48.3	*b,c*
Sm_2O_3	O_2	3.1	710	592	19.1	100	82.4	2.3	1.0	14.3	15.3	*c*
	N_2O	3.0	710	720	14.6	99	64.4	3.7	14.6	17.3	31.8	*c*
5% Li/Sm_2O_3	O_2	3.0	710	857	24.5	87	45.8	1.3	27.0	25.0	52.9	*c*
	N_2O	2.4	710	756	3.0	13	29.1	0	11.5	60.3	71.8	*c*
La_2O_3	O_2	4.6	550	3 660	2	25	—	—	0	0	0	*d*
	N_2O	4.6	550	3 660	tr.	4	—	—	0	57	57	*d*
	O_2	4.6	700	3 660	10	75	—	—	2	6	8	*d*
	N_2O	4.6	700	3 660	4	24	—	—	15	70	85	*d*
Sm_2O_3	O_2	4.6	550	3 660	11	93	—	—	1	10	11	*d*
	N_2O	4.6	550	3 660	0.5	5	—	—	3	82	85	*d*
	O_2	4.6	700	3 660	15	98	—	—	10	21	31	*d*
	N_2O	4.6	700	3 660	5	35	—	—	10	68	78	*d*

[a] Selectivities calculated on carbon basis. [b] Ref. 36. [c] Ref. 35. [d] K. Otsuka and T. Nakajima, *Inorg. Chim. Acta*, 1986, **120**, L27; K. Otsuka, *J. Jap. Pet. Inst.*, 1987, **30**, 385

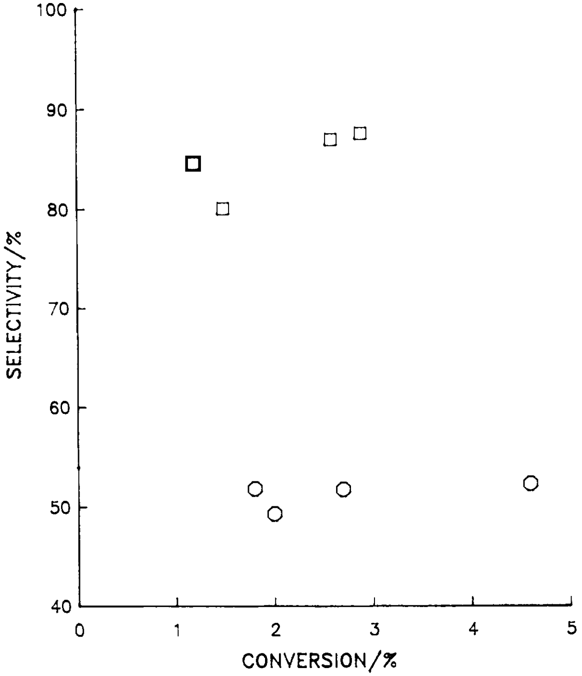

Figure 4 *Comparison of* C_2 *selectivity over* Li/MgO, 710 °C, CH_4/*oxidant* = 3: ○ O_2 *as oxidant*, □ N_2O *as oxidant, data taken from ref.* 20

oxidizing species may be slow, and experiments by the present authors have indicated that only partial N_2O decomposition occurs under most conditions.

N_2O has been utilized in these studies as a source of surface O^- as an oxidizing species[37] and some evidence for this is further obtained from the observation (Table 7) that with N_2O, CO is oxidized to CO_2 which is produced in significantly higher quantities than with O_2. Based on a detailed analysis of the reaction selectivities at 550 °C and 710 °C it has been shown[36] that O^- has two oxidizing roles on these catalyst systems, a selective oxidation role which is particularly marked at the lower reaction temperature, and a non-selective role which becomes significant at the higher temperature. The mechanistic significance of the comparison between O_2 and N_2O as oxidants will be discussed in more detail in Section 3.

C. Ozone as Oxidant.—Earlier studies reviewed by Foster[6] have indicated that ozone could, by virtue of its enhanced oxidizing activity, be active for methane oxidation at temperatures lower than those observed with molecular oxygen (*i.e.* <500 °C). A comparative study of ozone *versus* oxygen as oxidant[25] has shown

[37] C. Naccache, *Chem. Phys. Lett.*, 1971, **11**, 323.

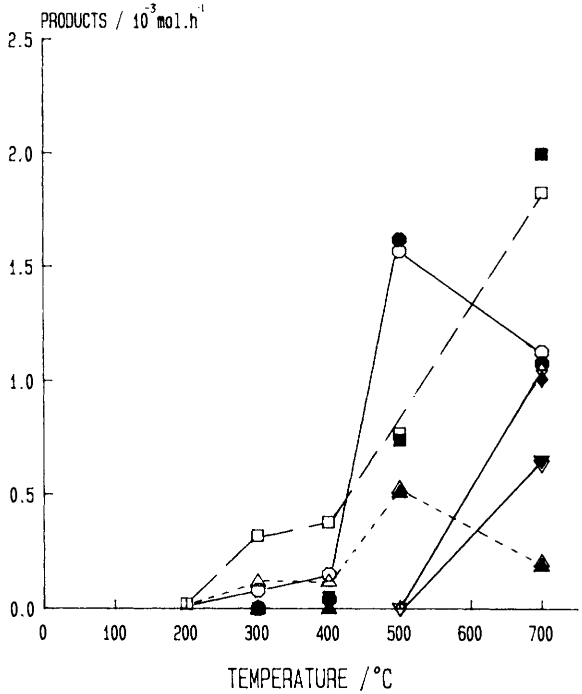

Figure 5 *Comparison of ozone and oxygen as oxidants over* Li/MgO: CH_4/*oxidant* = 3.3 *mole ratio.* 70 × 10^{-3} mol h^{-1} *inlet* CH_4 *Open symbols* O_3/O_2: 5 *mole* % O_3: *closed symbols* O_2: ◇ C_2H_6: ▽ C_2H_4: □ CO_2: △ CO: ○ H_2

that use of ozone does not enhance the production of either C_2 hydrocarbon or oxygenates at lower temperatures (Figure 5). Ozone was observed to be more reactive than molecular oxygen at <500 °C but the only products observed were hydrogen and carbon oxides.

D. Methane Oxidation in the Presence of Carbon Dioxide.—Aika and Nishiyama[27] have shown that addition of CO_2 to CH_4/O_2 reactant mixture can significantly enhance the yield of C_2 hydrocarbons for a broad range of catalysts, and in particular with PbO–MgO catalysts. It was concluded that the carbon dioxide was involved in these reactions as an oxidant, providing a monatomic oxygen species *via* degradation to carbon monoxide. However, no isotopic studies have been reported to substantiate the involvement of oxygen from carbon dioxide. It is more probable that the role of carbon dioxide is to enhance or maintain the formation of surface carbonate species which produces a more selective catalyst for methane activation. It is clear that further surface and isotopic studies are required to rationalize the experimental observations.

3 Studies of the Reaction Mechanism

A. The Role of the Alkali Promoter and Nature of the Active Site.—A number of studies have been made concerning the elucidation of the nature of the active catalytic sites particularly for the non-reducible oxide catalysts typified by MgO and Sm_2O_3, and particular attention has been given to establishing the role of the alkali promoter. Addition of Li^+ to MgO has been shown[38,39] to decrease the surface area, increase specific activity, both for methane oxidation and the selective production of C_2 hydrocarbons (Table 6), and significantly increase C_2 selectivity, particularly for C_2H_6. Even the addition of very low levels of Li^+ have been shown to exhibit these effects *e.g.* 0.4% by mass.[18]

Lunsford and co-workers[13,38,40–44] have extensively studied the Li/MgO catalyst using e.p.r. spectroscopy and have shown that in the presence of O_2 this catalyst forms O^- as a surface species, which is stabilized by the formation of $[Li^+O^-]$ sites. Previous studies of Abraham and co-workers[45–49] have demonstrated that $[Li^+O^-]$ centres can be found in Li^+-doped MgO or CaO, either by thermal treatment or by high intensity electron bombardment. Lunsford and co-workers[43] have further shown that gas phase methyl radicals were found when CH_4/O_2 were reacted over Li/MgO at 500 °C. Direct correlations were observed between the concentration of $CH_3^{\bullet}$ and the concentration of $[Li^+O^-]$ centres, as well as between the degree of methane conversion and the concentration of the $[Li^+O^-]$ centres. It was therefore concluded that the $CH_3^{\bullet}$ radical was produced from the interaction of CH_4 with the O^- of the $[Li^+O^-]$ centre.

The active $[Li^+O^-]$ was subsequently regenerated from the resultant LiOH by reaction of LiOH with molecular oxygen. For MgO, doping with Na^+ was not found to be as effective as Li^+. This has been explained in terms of the ionic radii of Li^+, Na^+, and Mg^{2+}. The $[Li^+O^-]$ centres are formed by substitution of Li^+ for Mg^{2+} in the MgO lattice and these ions have similar radii (Li^+ 68 pm, Mg^{2+} 66 pm). The larger Na^+ ion can not be so readily accommodated in the MgO lattice, and hence is less effective at generating the equivalent $[Na^+O^-]$ centre. However, Na^+ and Ca^{2+} also have very similar ionic radii (Na^+ 99 pm, Ca^{2+} 97 pm) and it is important to note that for CaO the most effective dopant is Na^+

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

[39] G. J. Hutchings, M. S. Scurrell, and J. R. Woodhouse, *J. Chem. Soc., Chem. Commun.*, 1987, 1862.

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[42] D. J. Driscoll and J. H. Lunsford, *J. Phys. Chem.*, 1985, **89**, 4415.

[43] D. J. Driscoll, W. Martir, J.-X. Wang, and J. H. Lunsford, *J. Am. Chem. Soc.*, 1985, **107**, 58.

[44] J. H. Lunsford, C.-H. Lin, J.-X. Wang, and K. D. Campbell, in 'Microstructure and Properties of Catalysts', ed. M. M. J. Treacy, J. M. Thomas, and J. M. White, *Mat. Res. Soc. Symp. Proc.*, Materials Research Society, Pittsburgh, 1988, **3**, 305.

[45] M. M. Abraham, Y. Chen, L. A. Boatner, and R. W. Reynolds, *Phys. Rev. Lett.*, 1986, **37**, 849.

[46] Y. Chen, H. T. Tohver, J. Narayan, and M. M. Abraham, *Phys. Rev. B*, 1977, **16**, 5535.

[47] J. B. Lacy, M. M. Abraham, J. L. Boldu, Y. Chen, J. Narayan, and H. T. Tohver, *Phys. Rev. B*, 1978, **18**, 4236.

[48] J. L. Boldu, M. M. Abraham, and Y. Chen, *Phys. Rev. B*, 1979, **19**, 4421.

[49] J. L. Olson, V. M. Orera, Y. Chen, and M. M. Abraham, *Phys. Rev. B*, 1980, **20**, 1258.

(Table 6), although both Li^+ and K^+ also significantly enhance the specific activity of CaO. Confirmation of the role of O^- in the selective oxidation of methane has come from photoluminescence studies[50] which have shown a direct correlation between the concentration of O^- on the surface of MgO and the conversion of methane. In addition, model studies using *X*-ray photoelectron spectroscopy on oxidized Mg for the analogous activation of N–H bonds in ammonia have also demonstrated the importance of the O^- species.[51] Use of N_2O as oxidant,[36] a known source of surface O^-,[37] has also confirmed the role of O^- in the selective oxidation of methane. Hence, there appears to be a general consensus that O^- on the surface of MgO and CaO, stabilized by the addition of Li^+ on Na^+, is the species responsible for the initial activation of methane *via* hydrogen atom abstraction to form a methyl radical. It must be noted that the presence of alkali cations is not crucial in this respect since undoped MgO and CaO are also active for methane partial oxidation.

The nature of the active centre on lanthanide oxide catalysts has been extensively studied. An e.p.r. study by Lunsford and co-workers[52] demonstrated that the rate of methyl radical formation was higher on La_2O_3 than on Li/MgO under comparable conditions. They found that superoxide, O_2^-, was the most abundant species and they considered that the broad e.p.r. spectrum of O_2^- might have masked the presence of O^-. It is interesting to note that doping La_2O_3 with Li^+ does not significantly enhance the specific activity (Table 6) which is in direct contrast to the effect of Li^+ on MgO and Sm_2O_3, and hence this could indicate that O^- may not be the active surface species for La_2O_3 oxide. However, it is clear that the methane activation on La_2O_3 is analogous to that on MgO and Li/MgO, *i.e. via* the generation of methyl radicals.

Otsuka and co-workers[34,53] have carried out a detailed kinetic study of Sm_2O_3 and have concluded that the active species for methane activation on this oxide is a diatomic oxygen species. Otsuka *et al.*[54] subsequently demonstrated that solid peroxides Na_2O_2, BaO_2, SrO_2 were active for the formation of ethane from methane in the absence of molecular oxygen. Based on these studies Otsuka has suggested that O_2^{2-} could be the active species on this oxide. More recently, Lee and Oyama[55] have noted that O_2^{2-}, which is difficult to characterize on an oxide surface, can be regarded as a dimer of O^-, *i.e.* O^-–O^-, and the formation of O^- from O_2^{2-} has been previously considered in the extensive reviews of Che and Tench.[56] Further evidence that O^- is the active species on Sm_2O_3 is provided by the observation that addition of Li^+ gives a significant increase in specific activity (Table 6) which is directly analogous to the effect of Li^+ doping on MgO. In addition, use of N_2O as oxidant in place of molecular oxygen (Table 7) significantly increases the formation of C_2H_6 at a decreased methane

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[50] M. Anpo, M. Sunamoto, T. Doi, and I. Matsuura, *Chem. Lett.*, 1988, 701.
[51] C. T. Au and M. W. Roberts, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 2047.
[52] C.-H. Lin, K. D. Kampbell, J.-X. Wang, and J. H. Lunsford, *J. Phys. Chem.*, 1986, **90**, 534.
[53] K. Otsuka and K. Jinno, *Inorg. Chim. Acta*, 1986, **121**, 237.
[54] K. Otsuka, A. A. Said, K. Jinno, and T. Komatsu, *Chem. Lett.*, 1987, 77.
[55] J. S. Lee and S. T. Oyama, *Catal. Rev.*–*Sci. Eng.*, 1988, **30**, 249.
[56] M. Che and A. J. Tench, *Adv. Catal.*, 1982, **32**, 77; *Adv. Catal.*, 1983, **32**, 1.

conversion. These effects of N_2O are similar to those observed with the Li/MgO catalyst, and hence by analogy it can be concluded that O^- is also the active oxidizing species on Sm_2O_3 and Li/Sm_2O_3.

Methane activation over reducible oxides, *e.g.* MnO_2, PbO, has not been studied in any particular detail. Keller and Bhasin[9] noted the active oxides for stoicheiometric methane activation had two accessible positive oxidation states, M^{n+} and $M^{(n-2)+}$, and they postulated the involvement of lattice oxide ions O^{2-} in the generation of activated surface methyl species. Subsequently Jones *et al.*[57] considered that the product distribution of C_2—C_6 hydrocarbon products was consistent with the involvement of gas phase methyl radicals in carbon–carbon bond formation. Driscoll and Lunsford[42] did not observe methyl radical formation in the CH_4/O_2 reaction over PbO at 475 °C whereas methyl radicals were observed over both MgO and Li/MgO at this temperature. It is clear that this aspect of methane oxidation requires further detailed study before any definitive conclusions can be drawn.

B. Primary Hydrocarbon Product Formation.—(i) *Identification of Primary Hydrocarbon Products.* Until recently only limited attention had been given in the research literature to consideration of the nature of the primary hydrocarbon products. This is surprising since without this detailed knowledge of the reaction mechanism it is unlikely that future improvements in catalyst design will be effected in a scientific manner. In part this is the result of early studies,[11,58] which concluded that ethane was the only primary hydrocarbon product and that the direct formation of ethene from methane was negligible. Subsequent studies have therefore worked on this basis, which is unfortunate since ethene is considered to be the more desired product on an economic basis and the identification and enhancement of a direct formation pathway would be a significant advance in catalyst design. A recent detailed study by the present authors[20,35,39] has shown that direct formation of ethene from methane is not negligible for all catalysts, and must therefore be considered in a mechanistic scheme. This investigation involved the standard procedure for determining primary selectivity by varying reactant feed-rate at constant reaction temperature and methane/oxidant ratio, both molecular oxygen and nitrous oxide were used as oxidants, and representative data are shown for MgO and Li/MgO in Figure 6. From this study it was concluded that for MgO, Sm_2O_3, and La_2O_3 with both O_2 and N_2O, and for Li/Sm_2O_3 with O_2, both ethene and ethane are the primary hydrocarbon products. For Li/MgO with O_2 and N_2O (Figure 6), Li/La_2O_3 with O_2,[35] and Li/Sm_2O_3 with N_2O[35] as oxidant the addition of Li^+ had a marked effect enhancing the formation of ethane relative to the unpromoted system. From these catalysts it was possible to conclude that ethane was a primary product, but the situation was less clear for ethene, since although linear extrapolation of the plots (*e.g.* Figure 6b) could have indicated a positive intercept for both ethane

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[57] C. A. Jones, J. J. Leonard, and J. A. Sofranko, *Energy and Fuels*, 1987, **1**, 12.

[58] K. Otsuka, K. Jinno, and A. Morikawa, *J. Catal.*, 1986, **100**, 353.

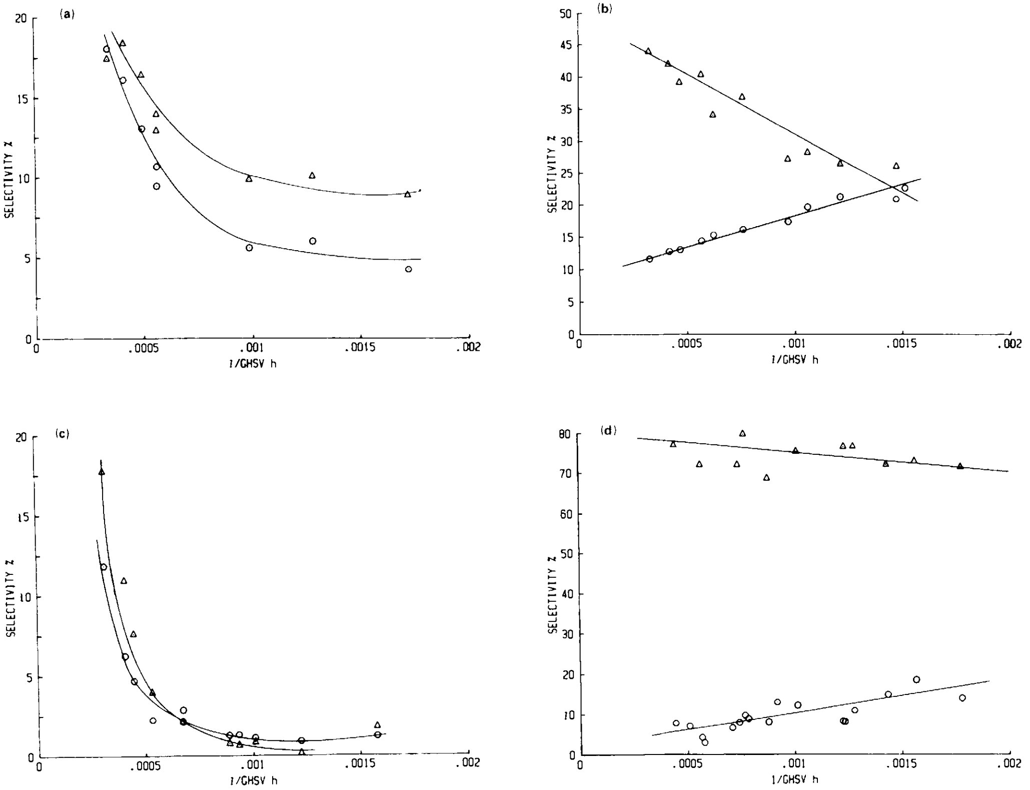

Figure 6 *Selectivity* versus *reciprocal gas hourly space velocity*; (a) MgO/O_2, (b) $Li/MgO/O_2$, (c) MgO/N_2O, (d) $Li/MgO/N_2O$; △ C_2H_6, ○ C_2H_4

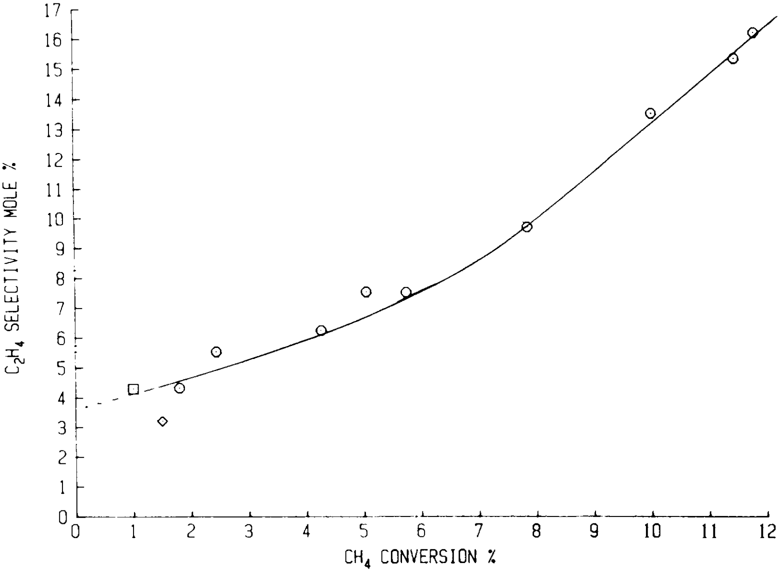

Figure 7 *Ethene selectivity as a function of* CH_4 *conversion:* Li/MgO; 710 °C; ○ $CH_4/O_2 = 3$ *mole ratio;* ◇ $CH_4/O_2 = 5$; □ $CH_4/O_2 = 10$

and ethene, it was possible that the shortest residence times used in these initial experiments may still have been too long to conclude that ethene was a minor primary product with these catalysts/oxidants. Further detailed studies[20,35] were then carried out with Li/MgO using a small catalyst bed volume (0.5 ml) with a minimized post reactor heated zone to limit the oxidative dehydrogenation of ethane downstream of the catalyst.[26] It was observed that for $CH_4/O_2 = 3$ a significant selectivity to ethene of *ca.* 4% was obtained on extrapolation to zero methane conversion (Figure 7), indicating that ethene selectivity and methane conversion is not linear in the conversion range of 0—10%, and in particular that extrapolation of data obtained for $\geq 5\%$ conversion could lead to a misleading conclusion concerning ethene as a primary product. This may have been the case in the earlier studies concerning primary product formation.[11,58] It was also shown[20] that decreasing the oxygen concentration did not significantly affect the ethene selectivity at low conversion while it did enhance the ethane selectivity, which indicated that the ethene primary selectivity was reasonably independent of the CH_4/O_2 ratio. It was observed that this finding strongly supported the conclusion that ethene was a primary reaction product, since if ethene were to be formed solely from oxidative dehydrogenation of ethane, as postulated in earlier studies,[11,55,58] then variation in $[O_2]$ would have been expected to affect the selectivity to ethene, and this was not observed. Based on this detailed study it was concluded that a small but significant primary selectivity to ethene could be observed for these catalysts. Hence for MgO, Sm_2O_3, and La_2O_3, with and without Li^+ and for both O_2 and N_2O as oxidants, a reaction pathway exists for the direct formation of ethene from methane and independent of C_2H_6.

(ii) *Mechanism of Primary Hydrocarbon Product Formation.* Based on the literature review in Section 3B(i) it is clear that both ethane and ethene must be considered as the primary hydrocarbon products, although for most catalysts ethane is the dominant primary product. There is general consensus[36,43,44,50,51,59] that surface O^-, derived from N_2O decomposition or stabilized by Li^+ doping, is the selective oxidizing species for ethane formation. Interaction of O^- with methane, either gas phase or surface associated (since recent studies[60,61] have indicated that significant amounts of methane are associated with some oxide surfaces even at 700 °C), leads to the formation of gas phase methyl radical *via* hydrogen atom abstraction. Cant *et al.*[62] have shown the existence of a kinetic isotope effect indicating that this hydrogen atom abstraction is the rate determining step in the formation of ethane. The radical nature of this reaction has been further confirmed in experiments using nitric oxide as a radical scavenger.[63] It is generally agreed that dimerization of methyl radicals leads to the formation of the ethane primary product, and this process occurs in the gas phase.

It has been noted[20,64] that the presence of Li^+ as dopant, which aids the stabilization of O^-, has significantly different effects on ethene and ethane selectivities, and from this observation it has been concluded that the surface O^- species cannot be the oxidizing species responsible for the formation of the ethene primary product. In addition it is probable that the primary formation of ethene must involve a surface-catalysed process since the diverse range of oxide catalysts give a wide range of primary ethene selectivities.[20,35,64] Recent studies by Martin and Mirodatos[65] have indicated that methylene carbene may be involved as a reactive intermediate in methane oxidation. They have postulated that the formation of the primary ethane product results from insertion of methylene carbene into a carbon–hydrogen bond of methane. Subsequent studies[66] using isotopic labelling have shown that this reaction does not occur. Oxidation of CD_4 and CH_4 mixtures resulted in the formation of ethane with isotopic distributions of CH_3–CH_3, CD_3–CD_3, and CH_3–CD_3; no ethane product containing CD_2 or CH_2 units were observed indicating that the methylene carbene species were not involved in the production of ethane. However, this species could be

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[60] A. Ekstrom and J. A. Lapszewicz, *J. Chem. Soc., Chem. Commun.*, 1988, 797.

[61] A. Ekstrom and J. A. Lapszewicz, *Prepr.-Am. Chem. Soc., Div. Pet. Chem.*, 1988, **33**, 430.

[62] N. W. Cant, C. A. Lukey, P. F. Nelson, and R. J. Tyler, *J. Chem. Soc., Chem. Commun.*, 1988, 766.

[63] G. J. Hutchings, M. S. Scurrell, and J. R. Woodhouse, *J. Chem. Soc., Chem. Commun.*, 1989, 765.

[64] G. J. Hutchings, M. S. Scurrell and J. R. Woodhouse, *Proc. 9th Int. Congr. Catal.*, Calgary, ed. M. J. Phillips and M. Ternan, Chemical Institute of Canada, 1988, **2**, 923.

[65] G. A. Martin and C. Mirodatos, *J. Chem. Soc., Chem. Commun.*, 1987, 1393; C. Mirodatos and G. A. Martin, *Proc. 9th Int. Congr. Catal.*, Calgary, ed. M. J. Phillips and M. Ternan, Chemical Institute of Canada, 1988, **2**, 899.

[66] P. F. Nelson, C. A. Lukey and N. W. Cant, *J. Phys. Chem.*, 1988, **92**, 6176.

involved in the primary formation of ethene *via* the following reaction pathways:

$$2\ddot{C}H_2 \longrightarrow C_2H_4 \qquad (1)$$

$$\ddot{C}H_2 + CH_3 \longrightarrow C_2H_5^{\bullet} \longrightarrow C_2H_4 + H^{\bullet} \qquad (2)$$
$$\qquad\qquad\qquad \hookrightarrow C_2H_6 + R^{\bullet}$$

It has been concluded,[20] on the basis of use of N_2O as oxidant or Li^+ addition to MgO, that methylene carbene could not be formed in significant amounts from an interaction of $CH^{\bullet}_{3(g)}$ with surface O^-, *i.e.* a second hydrogen abstraction. Hence it has been concluded that the oxidizing species responsible for methylene carbene formation, and consequently the primary ethene product, must be able to abstract two hydrogens from methane in a single interaction of methane with the surface. Detailed reviews by Che and Tench[56] have shown that oxide surfaces such as MgO are capable of stabilizing a range of oxygen species including superoxide O_2^- and peroxide O_2^{2-} in addition to O^-. From analysis of the experimental data[20] it was concluded that a dioxygen species, probably O_2^{2-}, is the most likely oxygen species responsible for the formation of the methylene carbene species. It is interesting to note that O_2^{2-} has been proposed by Otsuka[53,54] as an active oxidizing species for Sm_2O_3, a catalyst which gives significantly higher ethene selectivities than other oxides (Table 6).

C. Secondary Conversion and Non-selective Oxidation Reactions.—(i) *Secondary Conversion of Ethane to Ethene.* Ethene can be formed from the primary ethane product *via* two reaction pathways:

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2 \qquad (3)$$

$$C_2H_6 + \tfrac{1}{2}O_2 \longrightarrow C_2H_4 + H_2O \qquad (4)$$

For MgO, La_2O_3, and Sm_2O_3 it has been noted[35,64] that the selectivities of ethene and ethane are comparable at most reaction conditions. Hence the ethene/ethane ratio observed experimentally is close to that expected for thermodynamic equilibrium according to equation 3.[67] Hydrogen is a major reaction product for methane oxidation over undoped oxides which is consistent with this reaction. Subsequent studies[20] demonstrated that this non-oxidative pathway occurred only to a limited extent in the presence of an oxidant, and hence reaction 4 is the major pathway for secondary ethene formation under conditions of non-total oxidant conversion.

Only recently[20,68,69] have investigations been addressed at the relative rates of

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[67] R. Stull, E. F. Westrum, Jr., and G. C. Sinke, 'The Chemical Thermodynamics of Organic Compounds', John Wiley, New York, 1969.

[68] J. A. Roos, S. J. Korf, R. J. H. Veehof, J. G. van Ommen, and J. R. H. Ross, in Proceedings 1st Workshop on Catalytic Methane Conversion, Bochum 1988, *Catal. Today*, 1989, **4**, 441.

[69] J. W. M. H. Geerts, J. N. M. van Kasteren, and K. van der Wiele, in Proceedings 1st Workshop on Catalytic Methane Conversion, Bochum 1988, *Catal. Today*, 1989, **4**, 453.

oxidation of methane, ethane, and ethene. In general, as expected, ethane and ethene are oxidized far more rapidly than methane, a feature which has been neglected in some kinetic modelling studies.[28] Comparison of N_2O with O_2 as an oxidant for ethane has indicated[20] that N_2O is always more selective for ethene formation than O_2, and hence a monatomic oxygen species is the selective oxidizing species for this reaction. These studies[20,68,69] have all provided evidence that reaction 4 is a gas phase reaction and the presence of a catalyst only leads to enhance the parallel total oxidation pathway. However, these studies also indicate that reaction 4 is facile under the conditions required for methane partial oxidation and at high conversions, $>5\%$, it must be considered to be the major route for ethene production.

(ii) *Secondary Total Oxidation of Ethane and Ethene.* The mechanism of total oxidation of the C_2 primary hydrocarbon products has not been well studied. Lunsford and co-workers[70] have proposed that ethane is oxidized to carbon oxides *via* ethene and a direct pathway from ethane is not significant. However, no firm experimental evidence was provided in support of this hypothesis, and other studies have indicated that direct oxidation of ethane to carbon oxides occurs for Li/MgO[42] and Sm_2O_3.[58] From a detailed comparison of ethane oxidation by either O_2 or N_2O as oxidant[20] it has been concluded that the non-selective oxidation of ethane involves mainly a surface-catalysed reaction involving a dioxygen species, which was not identified and was designated as O_2^{n-}. A similar study[20] for ethene total oxidation also indicated the involvement of a dioxygen species, but in this case the reaction involved both surface catalysed as well as gas phase reactions.

(iii) *Non-selective Methane Oxidation and the Formation of Hydrogen.* Studies[36] have indicated that the surface O^- species has two distinct roles: (a) it is the selective oxidizing species responsible for the formation of methyl radicals, the precursor to ethane, and (b) it participates in non-selective methane oxidation—recent studies[20] have indicated this is *via* a parallel pathway to the selective methane activation route. Both of these pathways involve the surface species O^-. Studies have also shown[20,25] that N_2O and O_3/O_2 can react in the gas phase and in this case it is considered that a monatomic oxygen species is the reactive gas phase species. Recent studies[63] involving reaction in the presence of the known radical scavenger nitric oxide have indicated that a second oxidation species or site, separate from the surface species O^-, is also important in the total oxidation of methane. However this oxidation species/site has not yet been identified.

It is apparent that under most reaction conditions hydrogen is a major reaction product.[14,71] It is particularly marked for MgO as a catalyst (Table 6), but the selectivity to H_2 relative to that of C_2 hydrocarbons decreases on doping with Li^+. It can be considered that the increased surface concentration of O^-

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[70] H.-S. Zhan, J.-X. Wang, D. J. Driscoll, and J. H. Lunsford, *J. Catal.*, 1988, **112**, 366.

[71] J. A. Roos, A. G. Baker, H. Bosch, J. G. van Ommen, and J. R. H. Ross, *Catal. Today*, 1987, **1**, 133.

from doping with Li^+ results in oxidation of hydrogen to water. Roos *et al.*[71] considered that the hydrogen could result from a number of different pathways including: dehydrogenation of ethane, the water gas shift reaction, the decomposition of formaldehyde, and steam reforming reactions. In addition, hydrogen is well known as a reaction product from previous gas phase methane oxidation studies,[5] and Kimble and Kolts[72] account for hydrogen formation *via* decomposition of ethyl radicals to ethylene and hydrogen atoms, *i.e.* reaction 2. At the current level of definition it is possible to discount the significant involvement of ethane dehydrogenation, reaction 3, when unconverted oxidant is present. This has been shown by direct studies with ethane,[20] and in addition it is apparent that considerably more hydrogen than ethene is produced in the overall reaction (Table 6). It has also been observed[20] that the ratio of hydrogen and carbon oxides remains constant at variable contact time for a specific catalyst at constant temperature. The ratio H_2/CO_x was found to be dependent on the volume of the catalyst bed. It was concluded that a major pathway for hydrogen formation was from a reaction which is linked directly to the formation of carbon oxides. It was considered that a possible route was from the gas phase decomposition of oxygenated products, *e.g.* CH_3OH, CH_2O, formed from the reaction of $CH_3^{\cdot}$ or CH_2 with O_2 in the gas phase, *via* known reactions.[5] However, it is clear that a definitive study is still required to fully unravel the origin of hydrogen in this high temperature oxidation reaction.

D. Importance of Gas Phase Reactions.—A number of the individual reaction pathways considered in the preceding discussion are cited as involving gas phase reactions, rather than being wholly surface-catalysed. In particular, it appears that the prime function of the catalyst surface is to activate methane *via* interaction with a surface O^- species, which generates methyl radicals. These radicals are released into the gas phase and subsequently dimerize to form ethane or could react with oxygen to form the methyl peroxy radical which is a precursor for the formation of carbon oxides. Previous studies by Boomer *et al.*[15] have demonstrated that at high reaction pressures methane can be activated *via* a radical pathway in the absence of a catalyst acting as a radical initiator. It was therefore clear that the effect of increased reaction pressure in the catalysed methane oxidative coupling reaction should be evaluated. An initial study by the present authors[73] demonstrated that increasing reaction pressure from 85 kPa to 585 kPa negated the requirement for a catalyst, since at this pressure significant gas phase radicals can be thermally generated. It was noted that the presence of a catalyst could be deleterious since it tended to catalyse the non-selective pathways and hence decrease the yield of the desired products. Subsequent

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[72] J. B. Kimble and J. H. Kolts, *Chemtech*, 1988, 501.

[73] G. J. Hutchings, M. S. Scurrell, and J. R. Woodhouse, *J. Chem. Soc., Chem. Commun.*, 1988, 253.

[74] G. S. Lane and E. E. Wolf, *J. Catal.*, 1988, **113**, 144.

[75] D. Y. C. Yates and N. E. Zlotin, *J. Catal.*, 1988, **111**, 317.

[76] O.-T. Onsager, R. Lodeng, P. Soraker, A. Anundskaas, and B. Helleborg, in Proceedings 1st Workshop on Catalytic Methane Conversion, Bochum 1988, *Catal. Today*, 1989, **4**, 355.

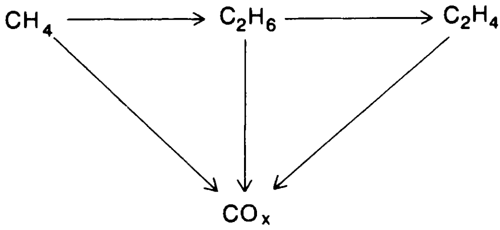

Figure 8 *Simple reaction network for the oxidation of methane*

studies[74–76] have confirmed these initial findings, and have demonstrated that gas phase reactions must be taken into account in the oxidative coupling of methane.[77] This is of particular importance with respect to the design of improved catalysts. Since if the overall activation of methane should be *via* the oxidative coupling reaction to ethane, with consecutive oxidative dehydrogenation to ethene, then based on current evidence it is probable that use of enhanced reaction pressure may yield the best results.

It is interesting to note that the enhancement in the selectivity to C_2 hydrocarbons observed on addition of LiCl to NiO, in comparison to the effect of addition of Li_2CO_3 or $LiNO_3$ (Table 3), may also be due to the involvement of gas phase reactions. It is possible that LiCl acts as a source of gas phase chlorine atoms that can initiate methane activation *via* hydrogen atom abstraction to form methyl radicals. The observation that catalyst lifetime is proportional to [LiCl] further confirms the direct involvement of the chloride in a non-catalytic mode. It is clear that further experimental work is required to elucidate whether chloride additives to catalysts (Tables 3 and 5) do have a true surface catalytic function. Recent studies by Burch *et al.*[78] have started to address this area and preliminary results indicate that surface reactions are involved in the production of ethene with chloride modified catalysts.

E. Overall Reaction Mechanism.—Most studies, summarized recently by Lee and Oyama[55] have concluded that a simplified reaction network can be utilized to describe the oxidative coupling of methane (Figure 8) and this has been used in various forms in a number of kinetic studies.[11,28,58] However, the present review of the current literature indicates that this level of simplification omits essential mechanistic details. Lunsford[70] has considered the reaction in more detail (Figure 9) and has postulated that reaction of a gas phase methyl radical with a surface oxide anion can lead to the formation of a surface methoxy intermediate which is involved in non-selective oxidation. However, the mechanistic proposal does not account for the direct oxidation of ethane to carbon oxides, nor does it consider the direct formation of ethene from methane. It is apparent that for the range of non-reducible oxide catalysts investigated to date (Tables 1—5) the

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[77] K. Seshan, *Appl. Catal.*, 1988, **44**, 275.

[78] R. Burch, E. M. Crabb, G. D. Squire, and S. C. Tsang, *Catal. Lett.*, 1989, **2**, 249.

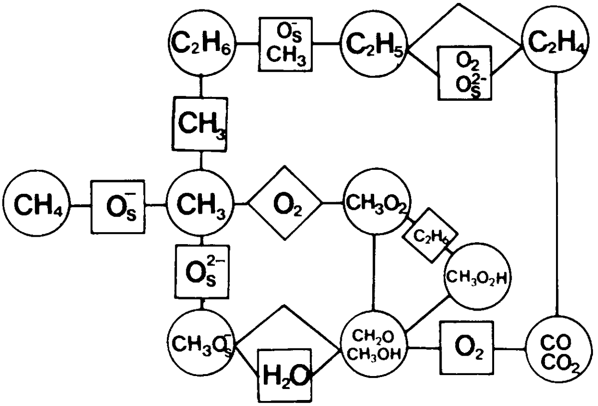

Figure 9 *Reaction mechanism for the oxidative coupling of methane*
(Reproduced by permission from *J. Catal.*, 1988, **111**, 302)

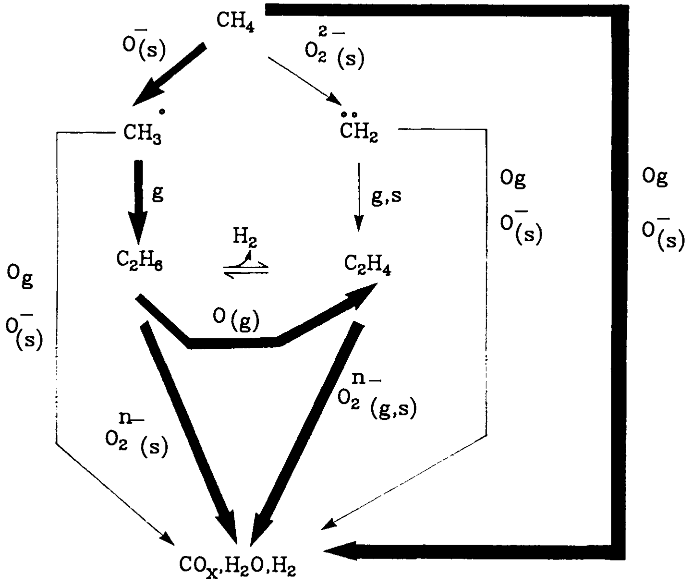

Figure 10 *Proposed reaction mechanism for the oxidative coupling of methane over non-reducible oxide catalysts*

products observed in all cases are broadly similar and comprise C_2H_4, C_2H_6, CO_2, CO, H_2, higher hydrocarbons together with H_2O and traces of oxygenates. Against the background of the reviewed literature and on the basis of a detailed study[20] the present authors have proposed a more detailed reaction mechanism of the oxidative coupling of methane (Figure 10). It is apparent that further study is required to fully characterize all the active oxygen species, but it is possible that the knowledge gained could be used as the basis for an approach to the design of an improved catalyst. For the oxides investigated to date the direct formation of ethene from methane occurs only as a minor pathway; it is clear, however, that Sm_2O_3 and Li/Sm_2O_3 demonstrate the highest primary selectivity to ethene.[35] In addition Li/Sm_2O_3 has been identified as having a specific activity for ethene formation that is over an order of magnitude higher than Li/MgO (Table 6). However, a detailed study of the surface characterization of Sm_2O_3 and Li/Sm_2O_3 has yet to be carried out. Such a study used in combination with similar studies for Li/MgO can be expected to be of value in the preparation of Sm_2O_3-based catalysts that exhibit improved ethene selectivity and activity.

4 Concluding Remarks

The aim of this review has been to highlight the most important aspects of the recent extensive literature concerning the oxidative coupling of methane to higher hydrocarbon products. In this respect a general mechanism for the methane oxidation over non-reducible catalysts has been described and discussed. A major feature of these oxides is that they only became active for carbon–carbon bond formation reactions at high temperatures (>700 °C) and at such temperatures it is clear that the gas phase nature of the overall reaction is dominant. Indeed, the use of increased reaction pressure can be more significant in effect than the use of the oxide catalysts described to date. However, it is also apparent that alkali-doped oxide catalysts exhibit a wide range of catalytic activities—a feature that has yet to be optimized. This, therefore, represents a major aspect identified in this review that is worthy of further detailed study. It is anticipated that an investigation of the solid state and surface chemistry of these doped oxides, together with optimization of the surface area, should provide the basis for the identification of improved activity catalysts containing an enhanced concentration of active surface sites. While the current studies indicate that use of increased pressure may be more effective, the use of a suitable catalyst will be of paramount importance in the control of the reaction selectivity. It is further suggested that significant efforts should now be given to the identification of oxide catalysts that are active for selective methane oxidation at lower temperatures (<500 °C) when surface reactions, in preference to gas phase radical chemistry, can be used to control selectivity to the desired product. A feature which is emphasized in this review is that specific oxygen species are responsible for both selective and non-selective oxidation. In particular, studies have indicated the existence of an oxidizing species or site that is involved specifically with total oxidation, but at the present it has not been identified. It can be expected that identification and control of this species or surface site could be of benefit in the preparation of improved catalysts.

The most striking feature of the wide range of catalyst evaluation studies reviewed in this article is that few general conclusions can be drawn from the vast body of data. This is primarily a result of the diverse reaction conditions employed by the different research groups involved. There is therefore a need to standardize the reaction conditions so that catalysts can be directly compared, and any advance in catalyst design can then be readily assessed. In particular, this comparison should be on the basis of specific activity data quoted for a range of operating temperatures.

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