The Role of Surface O^- in the Selective Oxidation of Methane

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For the title reaction $O^-_{(s)}$ is shown to have two distinct roles: at a low temperature $O^-_{(s)}$ acts *via* hydrogen abstraction to form ethane selectively and at high temperature it acts as a non-selective oxidant enhancing the formation of CO_2 and H_2O.

The oxidative coupling of methane to form ethene and ethane is currently the subject of considerable research interest. A number of oxide catalysts have been proposed for this reaction[1,2] and recently[3] the specific surface area has been shown to be important. In particular, catalysts based on MgO[4—6] and rare earth oxides[7—9] have given yields of C_2 hydrocarbons of up to *ca.* 70 mole %. At present most research effort has been directed at the identification of selective catalysts and the mechanism of selective methane activation has received limited attention. Lunsford[5] has observed that methyl radicals are formed which could subsequently dimerise to ethane, ethene being formed *via* oxidative dehydrogenation. Recently, studies of N–H and C–H activation with MgO[10] have indicated that surface methylene is formed in addition to methyl radicals. $O^-_{(s)}$ has been proposed[11,12] as the selective oxidant but as yet definitive catalytic data confirming these observations have not been presented. Here we present evidence, see Table 1, that $O^-_{(s)}$ can have two distinct roles in the oxidation of methane, which are dependent on reaction conditions.

Table 1

Expt.	Catalyst	Oxidant	CH_4/Oxidant mole ratio	T/K	GHSV[a]/ h^{-1}	CH_4 conv., mole %	Product selectivity,[b] mole% CO_2	CO	C_2H_4	C_2H_6	Total C_2
1	MgO	O_2	3.5	993	667	5.2	50.0	3.2	28.4	18.4	46.8
2	Li/MgO	O_2	3.3	993	648	2.7	33.0	1.6	26.5	38.9	65.4
3	MgO	N_2O	3.3	993	545	3.0	88.9	6.8	2.7	1.6	4.3
4	Li/MgO	N_2O	3.4	993	638	0.3	51.9	0	9.3	38.9	48.2
5	Ag/Al_2O_3	N_2O	3.8	993	556	2.0	90.5	8.5	1.0	0	1.0
6	MgO	O_2	3.5	823	667	3.0	66.2	31.8	0.4	1.6	2.0
7	Li/MgO	O_2	3.3	823	648	1.6	59.8	17.7	5.0	17.5	22.5
8	MgO	N_2O	3.3	823	563	1.8	96.1	2.0	0.3	1.6	1.9
9	Li/MgO	N_2O	3.4	823	638	0.2	17.2	0	7.0	75.8	82.8

[a] Gas hourly space velocity [volumetric gas flow rate/catalyst (1 ml)/h]. [b] Carbon containing product selectivity based on moles of CH_4 converted.

Reaction of CH_4/O_2 over MgO and Li/MgO at 993 K (expts. 1,2)† indicates that while MgO alone demonstrates significant C_2 selectivity (46.8%), addition of Li enhances the C_2 selectivity to 65.4% at the expense of methane conversion. The C_2H_4/C_2H_6 ratio indicates that MgO alone exhibits a higher oxidative dehydrogenation activity than Li/MgO. These results are in reasonable agreement with those previously described for Li/MgO.[4] To investigate the effect of $O^-_{(s)}$ at high temperature (993 K) on selectivity, addition of $O^-_{(s)}$ *via* N_2O was studied (expts. 3,4). N_2O is known to deliver $O^-_{(s)}$ on reaction with MgO.[12,14] For MgO and Li/MgO, a significant decrease in both activity and selectivity to C_2 hydrocarbons was observed. In addition a significant increase in the CO_2 relative to CO was observed. The results indicate that the role of added $O^-_{(s)}$ under such conditions is to enhance total oxidation activity, this effect being most pronounced on MgO. Confirmation of this effect is provided by results of experiments in which CH_4/N_2O was reacted over a Ag/Al_2O_3 catalyst (expt. 5), which is known[11] to generate $O^-_{(s)}$ from N_2O. The major product, as expected, was CO_2.

The effect of N_2O as an oxidant at low temperature (823 K) is mechanistically important (see expts. 6—9). For MgO alone, N_2O as oxidant in place of O_2 enhances the CO_2/CO ratio without significant effect on the C_2 selectivity or activity. For Li/MgO, an enhancement in the CO_2 relative to CO is also observed. However, a significant enhancement in total C_2 selectivity to 80 mole % (principally ethane) is observed, while activity is decreased by about one order of magnitude. Previous studies using O_2 as oxidant have not reported C_2 selectivities of this magnitude. From these results it is clear that the Li^+ in the MgO matrix plays a crucial role in stabilising $O^-_{(s)}$ generated from N_2O. This stabilised $O^-_{(s)}$ species selectively activates CH_4 to form C_2H_6 as the principle C_2 product and this is the dominant effect at low temperature. At a higher temperature the $O^-_{(s)}$ species enhances the total oxidation activity of the catalysts and CO_2 becomes the principle product. MgO alone cannot stabilise the $O^-_{(s)}$ species and consequently addition of $O^-_{(s)}$ to MgO, even at low temperature, enhances the total oxidation activity.

The results of this study therefore show that whilst $O^-_{(s)}$ is the selective species for the activation of CH_4 as previous studies[12] suggest, $O^-_{(s)}$ also has a second role which becomes more dominant at higher temperatures. In this situation the production of the undesired total oxidation products is enhanced. Stabilisation of $O^-_{(s)}$ (generated from N_2O) by Li^+ at low temperature leads to the observation of very high C_2 selectivities (80 mole %) but it is also apparent that Li/MgO cannot generate this species from O_2 at the lower reaction temperatures (expt. 7). Undoubtedly, the interplay between the two roles identified for $O^-_{(s)}$ in the oxidation of methane is complex and further studies in this area are now in progress.

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† MgO was prepared as previously described[13] and 5% Li/MgO was prepared using the method of Lunsford.[5] A 5% Ag/Al_2O_3 catalyst was prepared by impregnation of α-Al_2O_3 with aqueous $AgNO_3$, with the resulting solid being dried (50 °C, 16 h) and reduced *in situ* with hydrogen (400 °C, 18 h). Reactions were performed in a quartz microreactor (13 mm o.d.) at 823 and 993 K. CH_4/O_2 and CH_4/N_2O were individually reacted over the catalysts (4 ml) at conditions given in Table 1. Blank thermal reactions in the absence of catalyst were negligible under the conditions tested.