The Oxidative Coupling of Methane on Chlorinated Lithium-doped Magnesium Oxide

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The incorporation of chloride ions into Li-doped MgO, *via* a sol–gel process results in a stable and active catalyst that is capable of converting methane to ethylene through a series of partial oxidation reactions.

The oxidative coupling of methane to form higher hydrocarbons is an active area of research in catalysis and has been the focus of several recent reviews.[1] Recently there has been an emphasis on oxide catalysts promoted with chloride salts or gaseous chlorine-containing species.[2–5] The introduction of chlorine species into these catalysts increases the activity for methane conversion and can increase the ratio of ethylene-to-ethane in the products. Because of the utility of ethylene as a chemical feedstock it is desirable to maximize the conversion of methane to this particular product. Sofranko and coworkers reported a selectivity to C_2 and higher hydrocarbons of 90 at 30% CH_4 conversion by cofeeding HCl or MeCl with their reactants over a Na/Mn/Si based catalyst at 750–800 °C.[6] Burch *et al.*[7] reported C_2 selectivities of about 90% over a manganese dioxide catalyst doped with alkali chlorides and/or promoted with gaseous methylene chloride at 750 °C. Much of the work described thus far has been aimed at attaining higher conversions of methane with little mention of catalyst stabil-

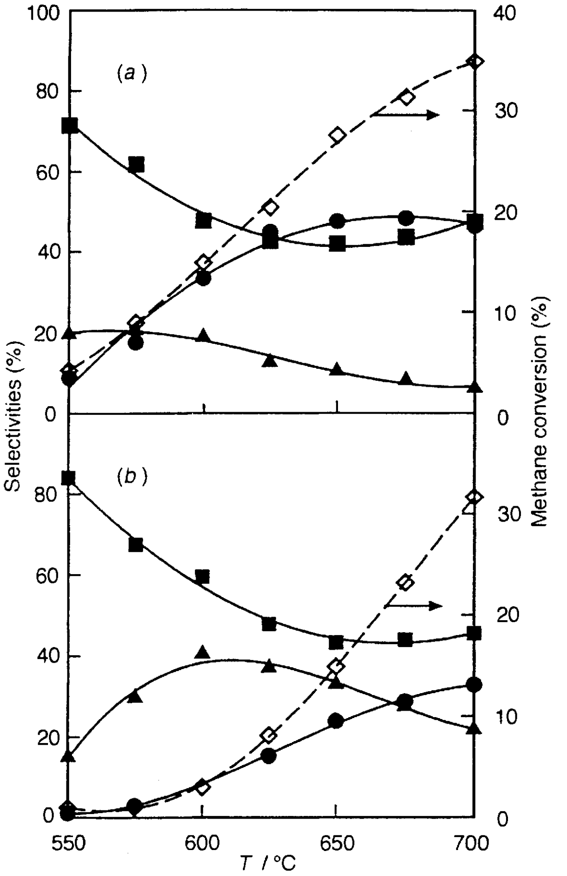

Fig. 1 Methane conversion and product selectivities as a function of temperature for (*a*) Li^+–MgO–Cl^- and (*b*) Li^+–MgO: ● C=C, ▲ C–C, ■ CO_2, and ◇ CH_4 conversion. The feed was 60 Torr of methane and 30 Torr of oxygen, the balance being helium at a total flow rate of 50 cm^7 min^{-1}. Because the apparent densities of the two catalysts were different, the mass of catalyst used was adjusted to give a bed volume of 7.7 cm^3 so that each experiment was carried out at the same space velocity. This resulted in the mass of Li^+–MgO used being 1.4 times the mass of Li^+–MgO–Cl^- used. The temperature was varied randomly.

ity. Here we report a comparison between a conventional Li_2CO_3/MgO catalyst and a chlorinated Li/MgO catalyst with regard to activity, selectivity and catalyst stability.

The catalyst designated Li^+–MgO–Cl^- was prepared using a sol–gel procedure that will be described in detail elsewhere.[8] A magnesium alkoxide was prepared by reacting magnesium metal with an alcohol in the presence of carbon tetrachloride, resulting in the incorporation of chlorine into the alkoxide solution. Lithium nitrate in ethanol was added to the alkoxide solution, and the mixture was gelled by bubbling water vapour (in nitrogen) through the mixture. The mixture was dried and then calcined as described below. The Li_2CO_3/MgO catalyst designated Li^+–MgO, was prepared from lithium carbonate and magnesium oxide by a slurry technique.[8] Both catalysts were calcined at 750 °C, sieved to 20/45 mesh and calcined again at 750 °C prior to use. Li^+–MgO–Cl^- and Li^+–MgO catalysts were prepared with a Li : Mg ratio of *ca.* 0.3, and for the Li^+–MgO–Cl^- catalyst the Li : Cl ratio was *ca.* 1. The catalytic experiments were carried out in flow reactors constructed from high purity alumina tubes of 1.95 cm inside diameter. The reactant gas mixture of methane, oxygen and helium (diluent) was introduced at a total flow rate of 50–55 cm^3 min^{-1} and a total pressure of 1 atm. A thermocouple well was located along the central axis of the reactor with the thermocouple at the centre of the 2.8 cm deep catalyst bed. At a nominal temperature of 650 °C, the bottom two thirds of the bed was 650 ± 2 °C, and the entrance of the bed was at 643 °C. The products were analysed by gas chromatography.

Table 1 Methane conversion, product selectivities, and C_2 yield over Li^+–MgO–Cl^{-a}

Time on stream/h	CH_4 conv. (%)	Selectivities (%)					C_2 Yield (%)
		C=C	C–C	CO_2	CO	C_3	
Feed CH_4/O_2 = 72/38 Torr							
26	33	47.0	5.8	36.1	11.1	0.0	17
91	37	45.1	7.8	43.2	0.0	3.8	20
104	34	46.8	8.5	44.7	0.0	0.0	19
120	37	44.4	8.1	47.5	0.0	0.0	19
180	36	42.1	8.9	46.4	0.0	2.4	18
Feed CH_4/O_2 = 303/155 Torr							
190	35	33.5	7.0	51.9	5.1	2.4	14
224	30	28.5	9.0	56.4	2.8	3.2	11
238	31	27.7	9.0	56.9	2.6	3.9	11

[a] *Conditions*: 6 g of Li^+–MgO–Cl^-, flow rate = 50 cm^3 min^{-1}, and T = 640 °C.

Fig. 1 shows the effect of temperature on methane conversion and product selectivity over Li^+–MgO–Cl^- and Li^+–MgO catalysts. The Li^+–MgO–Cl^- catalyst shows a greater activity for methane conversion, especially at the lower temperatures. At 550 °C, methane conversions of 4.3 and 0.96% were observed over the Li^+–MgO–Cl^- and Li^+–MgO catalysts, respectively. At 650 °C the conversions were 28% for Li^+–MgO–Cl^- and 15% for Li^+–MgO. The reaction became oxygen limited over Li^+–MgO–Cl^- at higher temperatures. The total selectivity to C_2 hydrocarbons (ethylene + ethane) was initially higher over Li^+–MgO–Cl^-, but was not substantially different at temperatures above 650 °C. The C_2 yield was higher for Li^+–MgO–Cl at all temperatures because of the greater methane conversion over this material. The most significant difference between the two catalysts is their relative selectivities to ethylene and ethane. As shown in Fig. 1 at temperatures above 575 °C the ethylene selectivity was greater than the ethane selectivity, and the selectivity to ethylene increased until the reaction became oxygen limited at the higher temperatures. Over the Li^+–MgO–Cl^- catalyst the ethylene : ethane ratio increased from 3.5 at 625 °C to 5.9 at 675 °C and from 0.4 to 1.0 for Li^+–MgO.

Methane coupling catalysts that contain chlorine suffer a loss of chlorine during reaction. Burch *et al.*[9] observed deactivation within 2 h on a $LiCl/MnO_2$ catalyst at 750 °C. Otsuka *et al.*[3] observed similar deactivation with a LiCl/NiO catalyst at 750 °C. However, when the reaction was run below 640 °C, the catalyst was stable for more than 20 h. Table 1 shows the results of an experiment in which a Li^+–MgO–Cl^- catalyst was kept on stream for 238 h at 640 °C. For the first 180 h the feed was kept at approximately 72 Torr of methane and 38 Torr of oxygen, with the balance being helium. The methane conversion varied from 33 up to 37% during this time. Although the ratio of ethylene to ethane decreased from 8.1 to 4.7, the total selectivity to C_2 hydrocarbons remained fairly constant at 51–53%. Under these conditions the catalyst was fairly stable, in contrast to the short lifetimes discussed above for other chlorine-containing catalysts. Increasing the partial pressure of reactants resulted in a decrease in the C_2 selectivity, but the catalyst remained active. The methane conversion only decreased from 35 to 31% over a 48 h period. During the 238 h on stream the catalyst lost approximately half of the lithium and chlorine initially present.

The incorporation of chlorine into lithium-doped magnesium oxide has two effects on the reactions involved in the oxidative coupling of methane. First, the Li^+–MgO–Cl^- shows a greater activity for methane conversion, even at lower temperatures. Significantly, at 650 °C the methane conversion was almost twice as great for Li^+–MgO–Cl^- as with Li^+–MgO. Second, the ethylene to ethane ratio is significantly enhanced. In agreement with these results recent work by Conway and Lunsford[10] suggested that the conversion of ethane to ethylene is enhanced over a Li^+–MgO–Cl^- catalyst relative to Li^+–MgO catalyst. They also found no correlation between the rate of HCl evolution and the rate of ethylene production, suggesting that there is very little conversion of ethane to ethylene by purely homogeneous reactions. Similarly, Burch and coworkers[9] concluded that ethylene selectivity was probably a result of heterogeneous reactions rather than gas-phase homogeneous reactions.

The chlorine appears to reduce the uptake of CO_2 and formation of bulk lithium carbonate in the Li^+–MgO–Cl^- catalyst. X-Ray diffraction (XRD) shows no bulk lithium carbonate formation on Li^+–MgO–Cl^- although X-ray photoelectron spectroscopy (XPS) shows features due to the carbon and oxygen of a near-surface carbonate. We have found that lithium-doped magnesium oxide catalysts prepared initially 'carbonate free' readily pick up carbon dioxide and form bulk lithium carbonate which is easily detected by XRD.[11] The work of Conway and Lunsford[10] confirmed that the chlorinated catalyst adsorbs much less CO_2. A more detailed account of the effect of chlorine on the lithium-doped magnesium oxide as a methane coupling catalyst will be given in a subsequent publication.

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