

The Effect of Nb₂O₅ and ZrO₂ Additions on the Behaviour of Li/MgO and Li/Na/MgO Catalysts for the Oxidative Coupling of Methane

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Incorporation of Nb₂O₅ or ZrO₂ into both Li/MgO and Li/Na/MgO systems produced ternary and quaternary catalysts, respectively, capable of attaining optimal C₂ yields and selectivities at lower temperatures relative to the unpromoted materials. The degree of enhancement effected by these metal oxide additives was compared to that produced by Li/MgO and Li/Na/MgO catalysts promoted with SnO₂ or Co₃O₄. At reaction temperatures < 700°C, the Li/Co/MgO ternary system showed marked differences in behaviour compared to the other ternary catalysts tested. This was particularly evident in the variation in C₂ selectivity with time on stream during ageing studies of (i) untreated materials, (ii) materials pretreated in CO₂, and (iii) materials dosed periodically with CHCl₃.

L'incorporation de Nb₂O₅ ou de ZrO₂ dans les systèmes Li/MgO et Li/Na/MgO produit des catalyseurs ternaires et quaternaires, respectivement, capables d'atteindre des rendements et des sélectivités de C₂ optimaux à des températures inférieures par rapport aux matériaux non activés. Le degré d'accroissement produit par ces additifs d'oxyde métallique est comparé à celui qui est produit par les catalyseurs de Li/MgO et de Li/Na/MgO activé avec du SnO₂ ou du Co₃O₄. À des températures de réaction inférieures à 700 °C, le système ternaire Li/Co/MgO montre des différences marquées dans le comportement comparativement aux autres catalyseurs ternaires testés. Cela est particulièrement évident dans la variation de la sélectivité du C₂ sur le courant au cours du temps dans les études de vieillissement (i) des matériaux non traités, (ii) des matériaux prétraités dans du CO₂ et (iii) des matériaux dosés périodiquement avec du CHCl₃.

Keywords: oxidative coupling, methane, Li/MgO, Li/Na/MgO, metal oxide additives.

The oxidative coupling of methane to higher hydrocarbons, principally ethylene, represents one of the alternate possibilities to that of well-established technology (Van der Wiele, 1986) whereby methane is converted to ethylene via syngas and methanol. The initial step in the latter process, involving steam reforming of methane to CO + H₂, requires high energy input at high temperature and hence proves to be considerably cost intensive. The production of higher hydrocarbons directly from methane is therefore highly desirable. Furthermore, with the advent of large worldwide reserves of natural gas which are often located in remote areas, direct on-site conversion of methane (the principal component) to light transportable fuels (derived from C₂H₄) is necessary to effectively offset current high transportation costs associated with shipping natural gas as a liquid or via pipelines.

These observations have fuelled the current intensive research campaign aimed at finding catalysts capable of oxidatively coupling methane to C₂ hydrocarbons with associated high yield and selectivity. Since the pioneering research (Keller and Bhasin, 1982) was carried out, a wide variety of promising catalytic systems have been developed including: Na-promoted PbO/γ-Al₂O₃ (Bytyn and Baerns, 1986), rare earth oxides such as Sm₂O₃ and Dy₂O₃ (Otsuka et al., 1985), NaMnO₄/MgO (Sofranko et al., 1987), and Li/ZnO (Matsuura et al., 1986). Since its emergence as one of the most active catalysts screened in this area (Ito et al., 1985), Li/MgO has remained at the forefront of the continuing research in this field. Optimisation of the catalytic potential of the material for the coupling process has centred around improving its activity (at lower reaction temperatures) and in particular its stability on stream. At the relatively high reaction temperature of 780°C required for optimal performance of the catalyst, deactivation occurs due to a progressive reduction in the number of active sites corresponding to a gradual loss of Li as volatile LiOH. A previous study

from this laboratory (Korf et al., 1989) showed that incorporation of oxides of Tb, Dy, Ti, V, Co, Ni, or Sn into Li/MgO resulted not only in a lowering of reaction temperatures required for attainment of optimal C₂ yields and selectivities but also considerably improved the on-line stability.

This follow-on study may be regarded within the same framework having the objective of investigating hitherto untested metal oxides as possible promoters not only for Li/MgO but also for the ternary Li/Na/MgO system. In the latter case, the presence of Na was intended to bring about a lower temperature melting of the Li₂CO₃ phase of the quaternary catalyst. The performance of Nb₂O₅ and ZrO₂ as promoters in these systems is considered in terms of a comparison with the promotional effects observed upon incorporation of SnO₂ or Co₃O₄ into both Li/MgO and Li/Na/MgO. As the behaviour of Co as an additive in both the ternary and quaternary catalysts proved to be somewhat different to the effects produced by the other additives employed, a low-temperature study of Li/Co/MgO is described which examines the ageing behaviour of the material in untreated form, following pretreatment in CO₂ and following periodic dosing with chloroform. For comparative purposes results from a similar set of experiments featuring Li/Nb/MgO are also presented.

Experimental

PREPARATION OF CATALYSTS

Li/X/MgO catalysts (X denoting metal oxide additive) were prepared as follows: Mg(OH)₂ was wet impregnated with LiOH at 80°C in a CO₂ atmosphere and subsequently dried at 125°C; the metal oxide was then added to the dried material and thoroughly admixed. The resultant catalyst was then calcined in air at 850°C for 4 h and subsequently

TABLE 1
Composition of Li/X/MgO and Li/Na/X/MgO Catalysts

Catalyst	Wt. % Li	Wt. % Na	[Li] (mmol/g)	[Na] (mmol/g)	[X] (mmol/g)
Li/MgO	1.3	—	1.87	—	—
Li/Nb/MgO(a)	7.0	—	10.01	—	0.93
Li/Nb/MgO(b)	6.1	—	8.79	—	1.11
Li/Zr/MgO	4.1	—	5.91	—	0.45
Li/Co/MgO	4.8	—	6.92	—	0.25
Li/Sn/MgO	6.0	—	8.57	—	0.20
Li/Na/MgO	3.3	3.7	4.75	1.61	—
Li/Na/Nb/MgO	5.3	7.1	7.61	3.07	0.41
Li/Na/Zr/MgO	5.0	5.3	7.13	2.31	0.29
Li/Na/Co/MgO	4.9	5.5	7.07	2.37	0.47
Li/Na/Sn/MgO	5.6	6.1	8.10	2.66	0.18

crushed and sieved to a grain fraction of 0.3 to 0.6 mm. Preparation of the Li/Na/X/MgO catalysts followed the same procedure with the initial step comprising wet impregnation of Mg(OH)₂ using a solution of LiOH and NaOH.

CHARACTERISATION OF CATALYSTS

Alkali metal content and metal oxide additive concentration were determined by AA and XRF analysis, respectively. Table 1 lists the series of ternary and quaternary catalysts used in this study. In general the concentration of the metal oxide additive was an order of magnitude lower than the concentration of alkali(s). Note the higher concentration of Li in the Li/X/MgO catalysts relative to the unpromoted Li/MgO material, and the higher concentration of Li + Na in the Li/Na/X/MgO catalysts compared to unpromoted Li/Na/MgO. This feature was particularly evident in the Nb promoted catalysts. This trend of greater retention of Li in the promoted systems indicated that an alkali — metal oxide additive interaction was taking place even under calcination conditions. XRD was performed on a Philips 1170 diffractometer employing Cu K α radiation of 1.5418 Å. Li₂CO₃ and MgO were the main phases detected in all Li/X/MgO systems, while Li₂CO₃, Na₂CO₃, and MgO constituted the principal phases present in the Li/Na/X/MgO catalysts.

EXPERIMENTAL CONDITIONS RELATING TO CATALYTIC TESTING

All catalysts were screened in a conventional continuous reactant flow system with on-line gas chromatographic analysis. A typical catalyst loading of 375 mg was secured between quartz plugs in a quartz reactor of 5 mm internal diameter and contacted with a gas feedstream of composition CH₄/O₂/He - 67/7/26 (vol%). Total reactant flow rate of 100 mL/min was employed to ensure ideal plug-flow conditions, thereby avoiding problems arising due to back mixing of reactants and products. Yield was calculated as conversion multiplied by selectivity. Both conversion and selectivity were calculated on the basis of carbon mole percent.

Results and Discussion

EFFECT OF ADDITION OF OXIDES OF Nb AND Zr ON THE CATALYTIC PERFORMANCE OF Li/MgO

Figure 1 illustrates the effects of incorporation of Nb or Zr on the performance of Li/MgO under both the standard

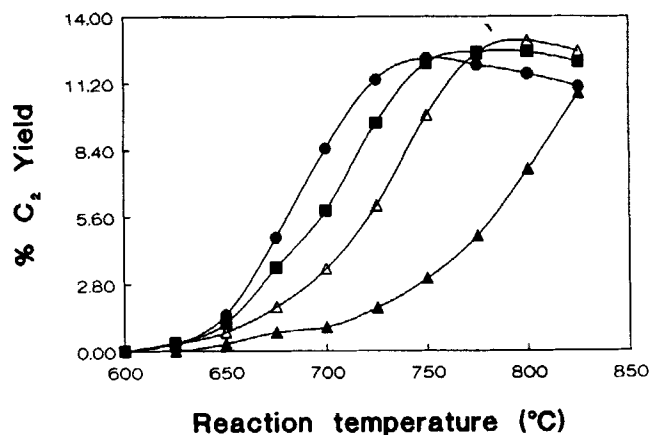


Figure 1(a) — Variation in % C₂ yield with reaction temperature under standard conditions of CH₄/O₂ = 9.6; Δ , Li/Ge/MgO; \triangle , Li/MgO; \blacksquare , Li/Zr/MgO; \bullet , Li/Nb/MgO.

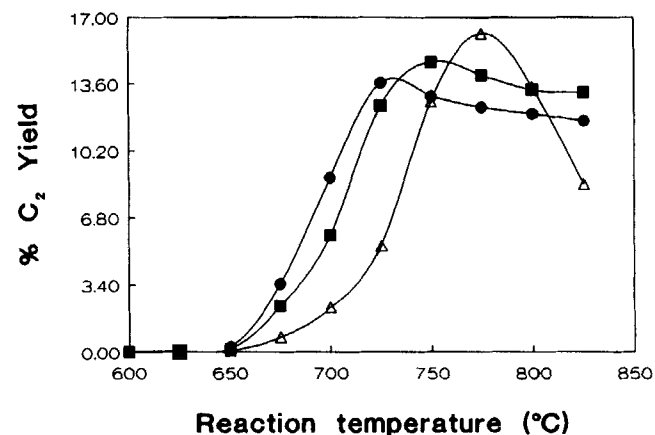


Figure 1(b) — Variation in % C₂ yield with reaction temperature under non-standard conditions of CH₄/O₂ = 5 and no He diluent; Δ , Li/MgO; \blacksquare , Li/Zr/MgO; \bullet , Li/Nb/MgO.

testing conditions of CH₄/O₂ = 9.6 (Figure 1a) and under reaction conditions more appropriate for industrial application, namely a lower CH₄/O₂ ratio and the absence of a diluent gas (Figure 1b). At the higher CH₄/O₂ concentration ratio, the presence of the metal oxide additives resulted in a shift to lower temperatures for attainment of optimal C₂ yields with the promoting effect of Nb emerging as superior to that of Zr. This trend of improved C₂ yields at lower reaction temperatures was due to higher CH₄ conversions on the ternary catalysts relative to Li/MgO. This implies

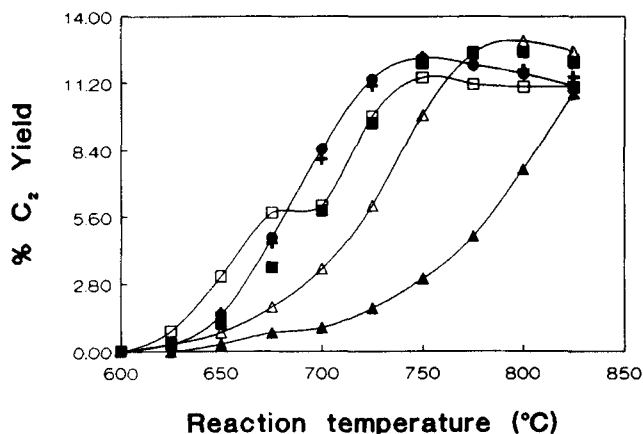


Figure 2 — Variation in % C₂ yield with reaction temperature under standard conditions for a series of Li/X/MgO catalysts: ▲, X = Ge; △, No X; ■, X = Zr; ●, X = Nb; +, X = Sn; □, X = Co.

that at temperatures $\leq 750^\circ\text{C}$, the total number of active sites on the promoted materials exceeded that on unpromoted Li/MgO; however, the nature of such sites can be said to be relatively unchanged because almost identical C₂ selectivity — temperature behaviour was observed between Li/Nb/MgO, Li/Zr/MgO, and Li/MgO. In contrast to the enhancing effects of Nb and Zr additives, incorporation of Ge as GeO₂ into Li/MgO resulted in poorer C₂ yields at all temperatures relative to the unpromoted material. The contrast between the detrimental effect of Ge addition and the promotional effect of other group IVA metal oxides, notably SnO₂ and PbO (Korf et al., 1989; Agarwal et al., 1990), may be seen as evidence supporting the concept that the alkali — metal oxide additive interaction is localised and selective.

Under conditions featuring a higher O₂ concentration in the feedstream, the enhancing effects of both Nb and Zr additives were also observed. In this case the performance of the Li/Zr/MgO system compared more favourably with that of Li/Nb/MgO, as highlighted by the closer correspondence of their respective profiles in Figure 1b compared to that in Figure 1a. (The conditions in Figure 1b were exactly the same as in Figure 1a and listed in experimental section, except for the fact that helium diluent was absent and CH₄ and O₂ made up the total flow of 100 mL/min and in the ratio 5:1). Under these reaction conditions, slightly better C₂ yields were obtained at temperatures $\geq 725^\circ\text{C}$ relative to the reaction conditions of Figure 1a. Comparison of the profiles for Li/MgO in Figures 1a and 1b indicated that in the latter case a dramatic change in behaviour was observed following attainment of maximum C₂ yield at 775°C. (The oxygen conversion around 800°C in these cases was between 85 to 90 mol%). This took the form of a rapid deactivation following the development of a hot spot within the catalyst bed (Korf et al., 1990). As no such similar deactivation was noted on either of the ternary systems, a further beneficial effect of the presence of Nb or Zr additives was ascribed to effective inhibition of hot spot formation under conditions of high O₂ concentration in the feed.

In order to qualify the extent of promotion observed on both Li/Nb/MgO and Li/Zr/MgO relative to that produced by other metal oxide additives, ternary catalysts Li/Sn/MgO and Li/Co/MgO were also screened under the standard conditions. The combined results are depicted in Figure 2. Both Li/Nb/MgO and Li/Sn/MgO exhibited similar behaviour at

each selected reaction temperature; note how both profiles essentially coincided over the entire 600 to 825°C temperature range employed. Although the Li/Zr/MgO system displayed the lowest degree of promotion (Li/Ge/MgO shows a negative effect and is not considered further) at temperatures $\leq 675^\circ\text{C}$, its performance improved with increasing temperature. It matched the performance of Li/Co/MgO at both 700 and 725°C, and subsequently gave the best C₂ yields of all the Li/X/MgO systems at temperatures $\geq 775^\circ\text{C}$. Indeed the promotional effects of each additive studied may be viewed in three distinct temperature regimes: from 600 to 675°C, Co was clearly the best additive, while from 700 to 750°C both Nb and Sn achieved the greatest degree of promotion, and finally at temperatures above 750°C, Zr proved to be the most effective additive.

Examination of the shapes of the profiles in Figure 2 reveals that whereas essentially sigmoidal curves were observed for Li/Nb/MgO, Li/Sn/MgO, and Li/MgO, the profile for Li/Co/MgO was characterised by a distinct plateau between 675 and 700°C. An investigation of this and other features, which clearly distinguished the behaviour of Co from the other additives employed, is described in a later section in the form of a low-temperature study of Li/Co/MgO. At this point mention must also be made of a further distinguishing feature of the Li/Co/MgO ternary system. This concerned the production of CO across the 600 to 825°C temperature range; whereas all the other Li/X/MgO systems produced CO at each reaction temperature and Li/MgO itself formed CO at and above 625°C, no CO was ever observed in the effluent stream of Li/Co/MgO. This may be attributed to the greater potential of isolated Co sites (compared to isolated Sn, Nb, or Zr sites) to facilitate direct oxidation of CO to CO₂ within the catalyst bed (Yu-Yao, 1975).

EFFECT OF ADDITION OF OXIDES OF Nb AND Zr ON THE CATALYTIC PERFORMANCE OF Li/Na/MgO

Incorporation of Na into Li/MgO was performed with the intention of forming a bi-alkali eutectic melt to facilitate a lower temperature melting of the Li₂CO₃ phase of the catalyst. This in turn was expected to lead to the generation of active sites, as proposed previously on Li/MgO (Korf et al., 1988, 1990), at lower reaction temperatures. On that basis, the presence of Na was expected to produce shifts to lower temperatures for attainment of optimal C₂ yields in a similar manner as previously observed upon addition of Nb, Sn, Zr, and Co. In actuality the activity of the Li/Na/MgO material fell below the activity of any of the Li/MgO materials tested. This may be appreciated by the fact that on Li/Na/MgO, a rather high reaction temperature of 825°C was required to obtain a value of C₂ yield comparable to that achieved on Li/MgO at the somewhat lower reaction temperature of 775°C. However, as illustrated in Figure 3, a considerable improvement in the performance of the Li/Na/MgO system was achieved by addition of the oxides of Nb, Sn, or Zr. In this case, the order of additive enhancement emerged as Nb > Sn > Zr. Whereas enhancements observed in the Li/X/MgO — Li/MgO comparison extended up to and including 750°C (Figure 2), the promotional effects of the oxides of Nb, Sn, and Zr were still operational at temperatures up to and including 800°C in the Li/Na/X/MgO — Li/Na/MgO comparison (Figure 3).

In contrast to the other metal oxide additives, incorporation of Co as Co₃O₄ into Li/Na/MgO resulted in a substantial

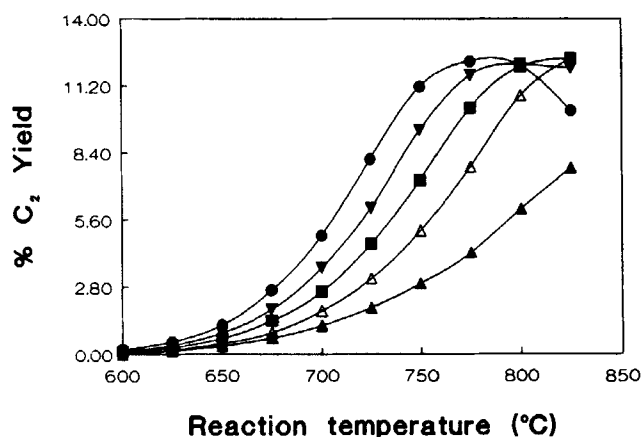


Figure 3 — Variation in % C_2 yield with reaction temperature for a series of Li/Na/X/MgO catalysts: ▲, X = Co; △, No X; ■, X = Zr; ▼, X = Sn; ●, X = Nb.

decline in activity across the temperature range employed. This further example of the unusual behaviour of Co as an additive may have been due to the formation of compounds such as Li-Na-Cobaltates which were not detected by XRD given the rather low concentrations of Co present in the quaternary catalyst. As a component of such a compound, any promotional effect of Co, as seen previously upon addition to Li/MgO, may have been effectively quenched. This being the case, no such compound formation would be anticipated on Li/Na/X/MgO materials (X = Nb, Sn, or Zr) since these elements showed only a promotional effect on the yield patterns. This further implies that the metal oxides may not be forming compounds as in the case of Co. Further characterisation of these materials is currently being carried out to clarify the precise nature of the interaction between the alkali(s) and the metal oxide additives used.

The quaternary Li/Na/X/MgO catalysts proved to be less active than their ternary Li/X/MgO counterparts. However, one beneficial effect of Na in controlling total oxidation was confirmed by comparing reaction temperatures at which CO formation commenced on Li/MgO and Li/Na/MgO. In the former case, CO was detected at a temperature as low as 625°C, but not until 775°C in the case of the latter material. (This would mean that the quaternary catalysts would be better in selective oxidation; indeed, they showed better C_2 selectivities, though the yields were smaller due to lower conversions).

AGEING EXPERIMENTS

Figure 4 illustrates the variation in C_2 yield with time on stream during ageing of Li/Na/MgO, Li/Na/Nb/MgO and Li/MgO at 750°C. The latter sample was calcined at a lower temperature of 700°C for 5 h to approach a Li content which was approximately equal to that of Li/Na/MgO. Prolonged ageing of the Li/Na/Nb/MgO material was not possible as the quartz reactors used invariably cracked, typically after 40 hours on stream. This was caused by erosion of the quartz, at the relatively high temperature of 750°C, by the large concentration of Li + Na in the catalyst; further ageing experiments are planned using an α - Al_2O_3 reactor. Comparison of the profiles revealed that whereas both Li/MgO and Li/Na/Nb/MgO tended to gradually deactivate with time on stream, a progressive improvement in the performance of the Li/Na/MgO material was observed over a 140 hour period. The deactivation observed in the former cases was

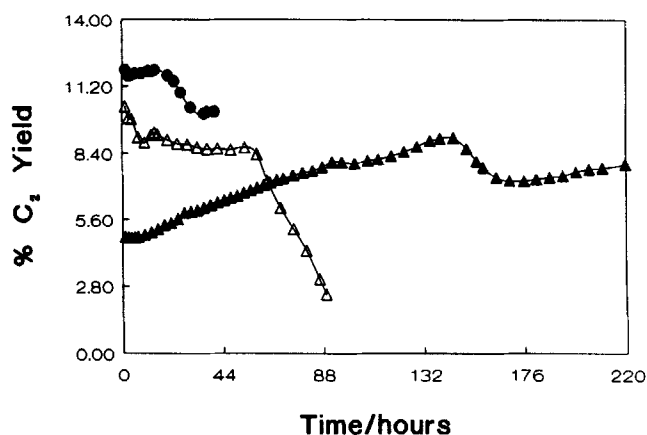


Figure 4 — Variation in % C_2 yield with time on stream during ageing of: △, Li/MgO; ▲, Li/Na/MgO; ●, Li/Na/Nb/MgO at 750°C.

attributed to loss of Li either by reaction with the quartz reactor for form Li_2SiO_3 or via volatilisation as LiOH. Although this reflected a decrease in the number of active sites, the nature of these sites can be said to be relatively unaffected from the fact that a constant C_2 selectivity of 80% on Li/MgO with time and a slightly lower but constant value of 75% on the quaternary catalyst was observed during measurements. Under these ageing conditions, a more gradual loss of Li would be expected on Li/Na/MgO given its poorer initial activity. Accordingly, the increase in the number of active sites on the catalyst (as reflected in improved C_2 yields at a constant C_2 selectivity of 82%) as a function of time on stream may be related to a gradual buildup of surface Li occurring as a direct consequence of its enhanced mobility in the form of volatile LiOH. This process would thereby give rise to a surface situation more characteristic of Li/MgO than of Li/Na/MgO where surface sites sustaining Na would be effectively covered by Li. Na/MgO is known to be a less active catalyst compared to Li/MgO, requiring temperatures approaching 800°C to attain high C_2 yields (Moriyama et al., 1986) and therefore coverage of Na sites by mobile Li would be expected to produce a more active catalyst. The decline in activity experienced by the Li/Na/MgO material after 140 hours ageing may be related to a progressive uncovering of Na sites following depletion of surface Li species to a level below that required for complete coverage of surface Na sites.

A LOW-TEMPERATURE INVESTIGATION OF THE Li/Co/MgO SYSTEM

Plateau effect

Of the series of ternary Li/Co/MgO systems presented in Figure 2, Li/Co/MgO was selected for the present investigation because: (i) it gave the best performance at reaction temperatures < 700°C and (ii) its profile was characterised by a distinct plateau between 675 and 700°C. The presence of the plateau was believed to reflect a re-distribution of surface species occurring in parallel with an enhanced mobility of Li within the aforementioned temperature range. The plateau became less pronounced on changing reaction conditions so as to introduce more O_2 into the feed stream. In fact at a CH_4/O_2 ratio of 5 and in the absence of He diluent, the plateau was no longer evident and the shape reverted back to that of the standard sigmoidal profile. One possible

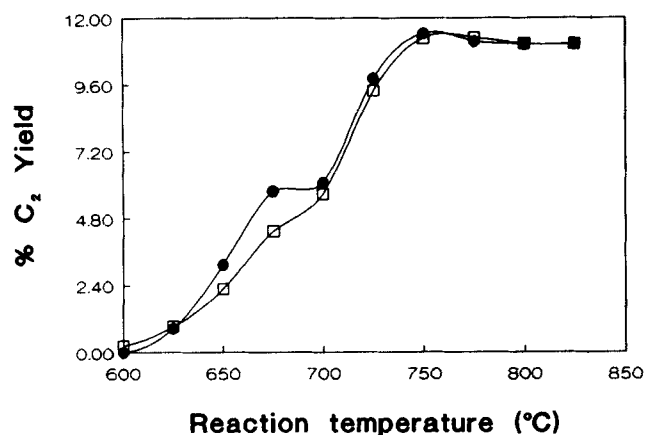


Figure 5(a) — Variation in % C₂ yield with reaction temperature of Li/Co/MgO in untreated form (●) and following pretreatment in CO₂/O₂/He (□).

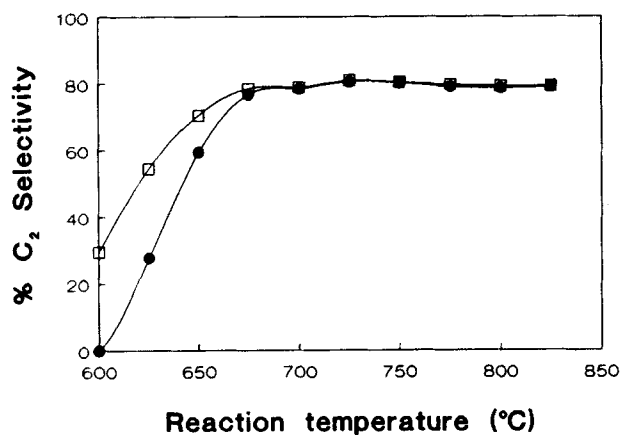


Figure 5(b) — Variation in % C₂ selectivity with reaction temperature of Li/Co/MgO in untreated form (●) and following pretreatment in CO₂/O₂/He (□).

interpretation of this trend centred around the optimisation of the promoting effect of Co while in the Co^{III} oxidation state. The latter would be expected to be more favoured at higher O₂ concentrations. TPO experiments are planned to investigate this possibility.

A series of tests was performed to investigate other possible modes of reversing the plateau effects. An effective procedure to emerge from this involved cycling the temperature between 600 and 700°C. During the heating stage the plateau was observed as before between 675 and 700°C; however, during the cooling stage it was effectively eliminated due to a reduced value of C₂ yield measured at 675°C. This loss in activity was attributed to a loss of Li from the catalyst (of the order of 15% of the initial Li content) during the cycling process. In contrast, no change in C₂ selectivity was recorded at 675°C between the heating and cooling stages, and furthermore upon cooling to 650 and 625°C improved C₂ selectivities were observed. This effect was related to a more severe retardation in CO₂ production relative to the observed decline in C₂ hydrocarbon production. The corresponding change in the nature of such surface oxidising sites may have been facilitated by an extensive spreading of mobile Li species across the catalyst surface resulting in a smaller concentration of bare Co sites thereon.

Examination of the profiles depicted in Figure 5a reveals that pretreating the Li/Co/MgO material in a flow of CO₂/O₂/He (20/7/13 Vol %) at 650°C for 16 hours proved

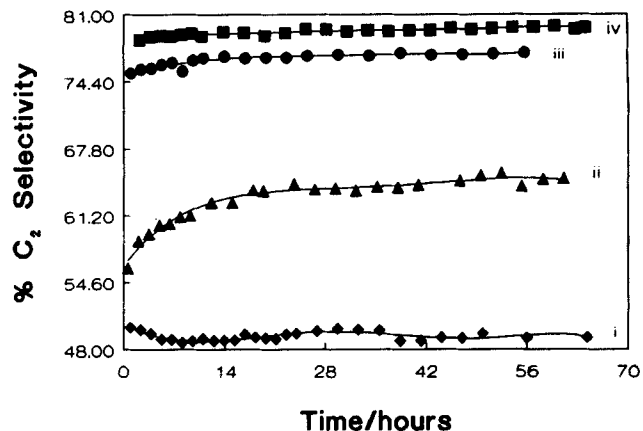


Figure 6 — Variation in % C₂ selectivity with time on stream during ageing of (i) Li/Nb/MgO at 660°C, (ii)-(iv) Li/Co/MgO at 650, 675 and 700°C.

to be another effective means of removing the characteristic plateau. The pretreatment in CO₂ also resulted in a slight poisoning of the catalyst at lower reaction temperatures; note the reduced values of C₂ yield on the CO₂ treated material at temperatures < 700°C. This poisoning was linked to the reduction of surface basicity accompanying carbonate formation. Above 700°C, the poisoning effect was no longer evident due to the loss of CO₂ from the catalyst simultaneous to the melting of the Li₂CO₃ phase (Korf et al., 1990). Figure 5b illustrates that at temperatures < 675°C a more selective catalyst resulted following the pretreatment in CO₂. This effect was qualitatively similar to that produced following the cycling of temperature between 600 and 700°C. In both cases, a more selective poisoning of sites responsible for CO₂ production compared to sites yielding C₂ products took place.

Effect of catalyst ageing at temperatures ≤ 700°C

The ageing behaviour of the Li/Co/MgO material within the temperature range extending from 650 to 700°C was examined next, and the corresponding profiles of % C₂ selectivity as a function of duration of ageing are represented in Figure 6. It is interesting to note that ageing at 650°C (line ii) was characterised by a gradual rise in C₂ selectivity from 56 to 64% over the initial 20 hours; subsequently constant behaviour was observed. Furthermore, under ageing conditions of CH₄/O₂ = 6.5 a similar effect was observed with the C₂ selectivity rising from 49 to 58% over a period of 22 hours. In contrast, ageing the Li/Co/MgO material at the higher temperatures of 675°C (line iii) and 700°C (line iv) or indeed a Li/Nb/MgO material at 660°C (line i) failed to exhibit a similar rise in C₂ selectivity during the initial period of ageing. In all three cases, constant C₂ selectivities of 75, 79, and 49%, respectively, were observed throughout the 60 hour ageing period. The different initial behaviour of the Li/Co/MgO material at 650°C was brought about by a progressive decline in the rate of CO₂ formation while the rate of C₂ formation decreased to a lesser degree (C₂ yield decreased from 2.8 to 2.3 during this period). At the higher ageing temperatures, the initial rate of decline in both CO₂ and C₂ formation was approximately the same; at 675°C, C₂ yield decreased from 5.2 to 4.8 during the initial 20 hours while a decrease from 6.3 to 5.6 was observed at 700°C over the same period. A tentative explanation of this trend again involved a mechanism of mobile Li spreading

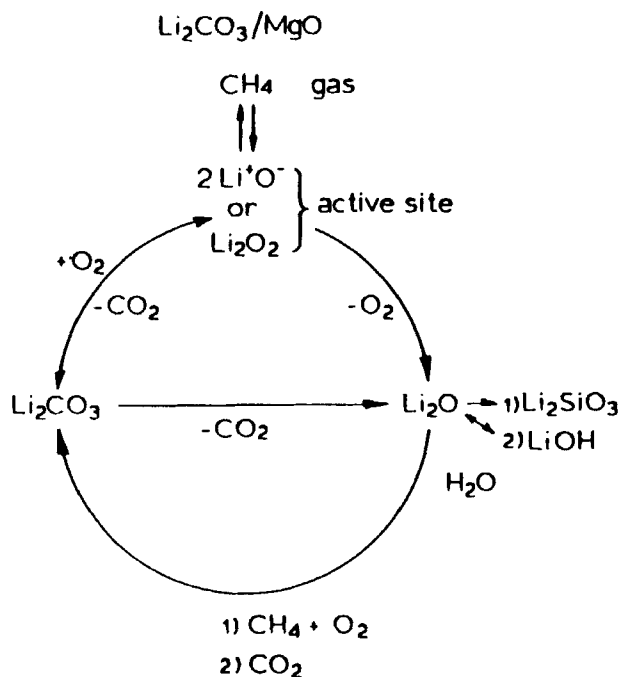


Figure 7 — Reaction network relating to the creation of active sites on catalysts based on Li/MgO.

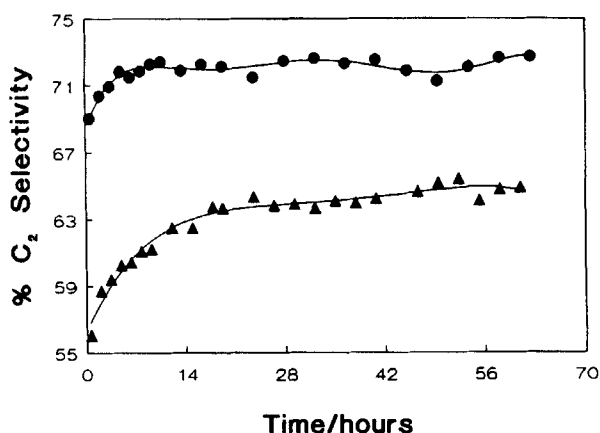


Figure 8 — Variation in % C₂ selectivity with time on stream during ageing at 650°C of Li/Co/MgO in untreated form (▲) and following pretreatment in CO₂/O₂/He (●).

across the surface. At the lower ageing temperature of 650°C, this process of changing the nature of surface sites was time dependent, whereas temperatures of 675 and 700°C were sufficiently high (pure Li₂CO₃ melts at 723°C) to cause a more rapid re-distribution of Li leading immediately to the surface situation generated only after 20 hours at 650°C.

Ageing behaviour following pretreatment in CO₂

A previous study from this laboratory (Korf et al., 1987) demonstrated that: (i) high temperature (780°C) pretreatment of a somewhat deactivated Li/MgO catalyst in CO₂ was a means of temporarily restoring the initial behaviour of the catalyst; (ii) active sites are created on the surface of the catalyst by the gradual loss of CO₂ accompanying the breakdown of surface Li₂CO₃ in the presence of O₂ as represented in the scheme of Figure 7; (iii) incorporation of CO₂ into the CH₄ + O₂ feedstream resulted not only in a

reversible poisoning of active sites but also stabilised them against deactivation. With this background, the ageing behaviour of a Li/Co/MgO material was examined at 650°C following a 16 hour pretreatment in CO₂ at the same temperature. Although this produced a less active catalyst relative to an untreated sample (due to the poisoning effect mentioned in (iii) above) comparison of the profiles in Figure 8 reveals a dual effect of the pretreatment in CO₂. Firstly, a considerably more selective catalyst was produced and secondly, the rise time associated with the attainment of maximum selectivity was shortened. It should be noted that pretreatment of the Li/Co/MgO material in a 50/50 mixture of O₂/He, but without CO₂, resulted in a catalyst identical to an untreated sample in terms of yield and selectivity. As CO₂ has been shown not to affect the selectivity of unpromoted Li/MgO (Korf et al., 1988) it may be postulated that in the case of Li/Co/MgO a more selective poisoning of Co-based total oxidation sites on the catalyst occurred during pretreatment in CO₂ and this in turn produced a more selective catalyst.

In order to qualify the observed effect of pretreatment in CO₂ on the selectivity of Li/Co/MgO, a Li/Nb/MgO catalyst was pretreated in CO₂/O₂/He at 660°C and subsequently aged at the same temperature. Essentially no difference in behaviour in terms of C₂ yield and selectivity was found between an untreated sample of the ternary material and the aliquot pretreated in CO₂. In a similar manner, ageing of a Li/Sn/MgO catalyst at 650°C was also found to be relatively independent of pretreatment in CO₂. It should be noted that both Li/Nb/MgO and Li/Sn/MgO materials in untreated form or following pretreatment in CO₂ exhibited better on-line stability relative to Li/Co/MgO in untreated form or pretreated in CO₂ respectively.

Ageing behaviour following dosing with CHCl₃

Although the use of Cl₂ or chlorine-based oxidising agents such as HCl as the oxidant in the methane coupling process is not industrially attractive due to inherent corrosion problems, nevertheless recent studies (Burch et al., 1989, 1990; Ahmed and Moffat, 1989) have demonstrated that addition of trace amounts of HCl or chloromethanes such as CH₂Cl₂ produces some beneficial effects. The latter may be best described as facilitating improvements in the C₂H₄/C₂H₆ ratio coupled with inhibition of the deep oxidation of CH₄ on a range of catalysts including MnO₂, Sm₂O₃, Li/MgO and Ba/SiO₂. In the light of these results, periodic injection of 5 μL of CHCl₃ was made to a Li/Co/MgO catalyst being aged at 655°C. The corresponding effects on both C₂ yield and selectivity are illustrated in Figures 9(a) and 9(b), respectively. The trend in both figures was essentially the same and may be interpreted as follows: subsequent to each of the first two CHCl₃ doses, slight decreases in C₂ yield and selectivity occurred. However, in the interval between these injections, C₂ selectivity recovered to re-attain pre-dosing values, while C₂ yield did somewhat better in surpassing pre-dosing values. Following injection three and subsequent injections a similar pattern emerged. This took the form of a sharp enhancement in both C₂ yield and selectivity coupled with an improved ethene to ethane ratio immediately following dosing with CHCl₃ to be followed by a rapid deactivation. The degree of this short-lived enhancement became more pronounced with the number of doses made while the extent of catalyst recovery between doses declined. A similar picture in terms of variation in both C₂

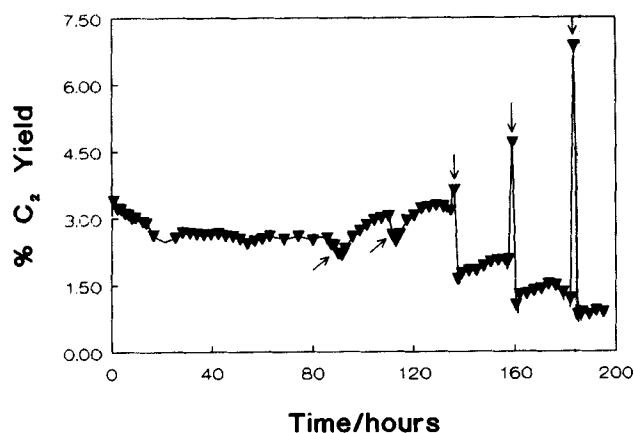


Figure 9(a) — Variation in % C_2 yield with time on stream during ageing of Li/Co/MgO at 655°C featuring periodic dosing with chloroform (indicated by arrows).

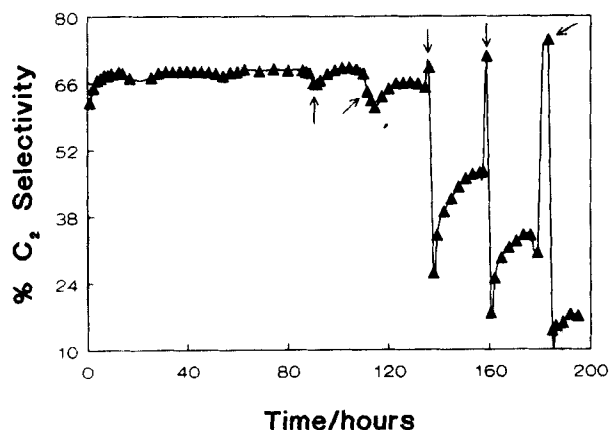


Figure 9(b) — Variation in % C_2 selectivity with time on stream during ageing of Li/Co/MgO at 655°C featuring periodic dosing with chloroform (indicated by arrows).

yield and selectivity was obtained during $CHCl_3$ dosing of another sample of Li/Co/MgO. The latter material (calcined at 700°C) proved to be more active though less selective than the material of Figures 9(a) and 9(b). This emphasises that the effect of $CHCl_3$ dosing on the Li/Co/MgO system was relatively independent of the preparation of the material. The behaviour of the ternary system as per Figures 9(a) and 9(b) was interpreted in terms of the production of a reaction front of volatile LiCl within the catalyst bed. This resulted in the development of a transient surface situation whereby Co-based total oxidation sites were temporarily blocked by Li-based species. This in turn produced the observed momentary enhancements in catalytic activity. The subsequent rapid deactivation was attributed to an aggravated loss of Li following progression of the LiCl front (under the influence of the reactant flow) downstream of the catalyst bed. The gradual recovery of the catalyst between injections was related to the possibility of a gradual loss of more strongly-bound Cl species (occupying oxygen vacancies for instance) with concomitant re-oxidation of the catalyst.

Preliminary $CHCl_3$ dosing experiments on a Li/Nb/MgO material being aged at 660°C revealed less dramatic effects than those observed in the case of Li/Co/MgO. A 5% increase in C_2 selectivity (due to a suppression in both CO and CO_2 formation) was measured directly following the first $CHCl_3$ dose, while no change occurred in the overall C_2 yield. In contrast to the findings of Burch et al. (1990)

on MnO_2 catalysts and Ahmed and Moffat (1989) on oxides of Ba, Cs and Mn supported on SiO_2 , introduction of the chloromethane in this case did not give rise to an improved C_2H_4/C_2H_6 ratio. In fact, the opposite trend was observed. This difference may be a consequence of the fact that reaction temperatures in the present investigation were at least 100 degrees lower than in the aforementioned studies. Accordingly, a greater catalytic role would be anticipated in the present case. Upon performing a second $CHCl_3$ dosing of the Li/Nb/MgO material, a further 2.5% rise in C_2 selectivity was noted with C_2 yield remaining relatively constant. As a further improvement in performance was recorded on the subsequent analysis (indicating a memory effect of the $CHCl_3$ dosing on the catalytic surface) a third injection of $CHCl_3$ was made 3 h after the second. This caused a slight reduction in C_2 yield without affecting C_2 selectivity. Loss of Li as LiCl (which was identified as the white deposit in the post catalytic volume of the reactor) was deemed responsible for this slight deactivation. Further experimental investigation of the effects of $CHCl_3$ dosing on a wider range of ternary Li/X/MgO systems is currently in progress.

Conclusions

The addition of Nb_2O_5 or ZrO_2 to Li/MgO produced ternary catalysts which were more active than and as selective as the unpromoted material. The greater activity was manifested in a shift to lower temperatures for attainment of optimal C_2 yields. A similar promotional effect was observed following incorporation of these oxides into Li/Na/MgO and furthermore remained operative to higher temperatures.

In the low-temperature regime of 650–700°C, the ternary Li/Co/MgO system was distinguished from Li/Nb/MgO in a number of respects. A more selective Li/Co/MgO catalyst was obtained at 650°C, either during the initial period of ageing, or more directly following pretreatment in CO_2 . This effect was related to surface re-distribution phenomena resulting in a more severe deactivation of Co-based total oxidation sites compared to sites responsible for C_2 production. Periodic, $CHCl_3$ dosing of the material, during ageing at 655°C, resulted in transient improvements in performance followed by pronounced deactivation; the latter effect was associated with a more severe loss of Li as volatile LiCl.

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