

Oxidative Coupling of Methane over Ba/CaO Catalysts

A Comparison with Li/MgO

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ABSTRACT

A comparison has been made of the behaviour in the oxidative coupling of methane of a Ba/CaO catalyst with that of a Li/MgO material. Doping of CaO with BaCO₃ resulted in a catalyst which is more active at lower reaction temperatures than is BaCO₃. The active oxygen entity in the case of Ba/CaO is probably an O₂²⁻ species. Ba/CaO is more stable but less selective than is Li/MgO. The effect of residence time was studied for both Ba/CaO and Li/MgO. The direct oxidation of methyl radicals to give carbon monoxide and carbon dioxide plays a more important role in the case of Ba/CaO than is the case with Li/MgO.

INTRODUCTION

The oxidative coupling of methane to given ethane and ethene has attracted increasing interest over the last few years. Examples of interesting catalyst systems which have been studied to date are: Mn₂O₃ supported on SiO₂ [1,2], PbO supported on Al₂O₃ [3] or MgO [4], Sm₂O₃ [5] and Li-doped MgO [6] (hereafter referred to as Li/MgO).

We have recently presented results leading to a possible model for the reactions which occur on the surface of a Li/MgO catalyst [7]. Active sites are created on the surface in the presence of oxygen by the gradual loss of carbon dioxide from surface lithium carbonate species. The active sites created are not stable but disappear as a result of the loss of lithium by volatilisation of LiOH as well as by the formation of Li₂SiO₃. The presence of carbon dioxide in the gas feed has two effects: namely, to poison reversibly the active sites for the oxidative coupling reaction but also to stabilise them against deactivation.

In an attempt to find catalysts with which the active component is not lost

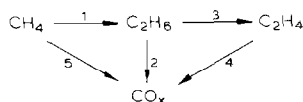


Fig. 1. General reaction scheme for the oxidative coupling of methane to ethane and ethylene.

during reaction, we have carried out a study of the use of the more stable carbonate, BaCO_3 , supported on $\text{Ca}(\text{OH})_2$, this material being referred to as Ba/CaO. We chose BaCO_3 for study because BaCO_3 cannot be volatilised under the reaction conditions for methane coupling; it is also known from the literature [8] that O_2^{2-} ions are easily formed on BaO, these species being possible active sites for methane coupling. The results for this system are reported below where they are compared with those for a Li/MgO catalyst.

In the oxidative coupling of methane to give higher hydrocarbons, it is important to suppress kinetically the rates of formation of carbon oxides relative to those of the desired products as the formation of carbon oxides is thermodynamically more favourable. A general reaction scheme for the reactions leading to the formation of ethane, ethene and total oxidation products, CO_x (i.e. carbon monoxide and carbon dioxide) is shown in Fig. 1; this is a network in which CO_x may be formed both directly from the reactant methane (i.e. parallel to the desired reaction) as well as from the C_2 products (i.e., a consecutive path). It is important to gain a clear idea of the relative importance of each of these steps as such an understanding might lead to the development of more selective catalysts. Using a continuous stirred tank reactor (CSTR) [9], we have shown that the reactions taking place during the oxidative coupling of methane over Li/MgO at 720°C occur predominantly as follows: $\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 \rightarrow \text{CO}_x$. A possible reaction network for Ba/CaO and Li/MgO catalysts has also been examined in the work reported in this paper by varying the residence time in a plug-flow reactor.

EXPERIMENTAL

Catalyst preparation

Preparation techniques such as wet impregnation of CaO with $\text{Ba}(\text{NO}_3)_2$ or coprecipitation of $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$ with $(\text{NH}_4)_2\text{CO}_3$ resulted in catalysts whose catalytic behaviour in preliminary experiments did not differ much from that of materials prepared simply by wet mixing of BaCO_3 and $\text{Ca}(\text{OH})_2$. In all cases, the catalysts were dried at 140°C and calcined in air at 850°C (6 h). The fact that the preparation technique has little or no influence on the resultant Ba/CaO catalyst is probably caused by the relatively high calcination temperature used. The results given in this paper were obtained using the Ba/CaO catalysts prepared by wet mixing and by wet impregnation. The Li/MgO

(B) and K/MgO catalysts, which were used for comparison purposes, were prepared by wet impregnation of MgO [7]. All the catalysts were crushed and sieved to a grain size of 0.3–0.6 mm before use.

Catalyst analysis and characterisation

Elemental analysis was carried out with atomic absorption spectroscopy (AAS) and X-ray fluorescence (XRF). X-ray powder diffraction (XRD) was carried out with a Philips PW 1710 diffractometer using Cu $K\alpha$ radiation and surface areas were determined using argon adsorption. The decomposition of the carbonate species on the barium-doped samples was measured using a temperature-programmed decomposition system (TPD); this was equipped with a thermal conductivity cell in which the sample was heated at a constant rate (14 °C/min) in a stream of helium. Water vapour was condensed out of this system after the reactor using a cold trap maintained at –30 °C. The carbonate contents were determined by wet analysis using the Blom–Edelhausen method. Fourier transform infrared (FTIR) measurements of self-supporting disks of the barium samples were carried out with a Nicolet 20 SXB spectrometer.

Catalytic experiments

The catalytic experiments were carried out in reactors made of quartz or fused Al_2O_3 with an internal diameter of 4 mm. The gas feed consisted of methane (0.67 bar), oxygen (0.07 bar) and helium (0.26 bar). The gases were analysed by gas chromatography [10]. The effects of BaCO_3 content and helium pretreatment were measured with catalyst weight $W=0.375$ g and gas flow $F=1.67$ cm³ (STP) s⁻¹; these conditions avoided the formation of hot spots under plug flow conditions [11]. The effect of W/F was studied with a constant value of F of 1.67 cm³ (STP) s⁻¹ by variation of catalyst weight W . The ageing of the catalysts was studied with a 0.750-g sample with a value of F of 3.33 cm³ (STP) s⁻¹. The measurements with BaO_2 were carried out in a fused Al_2O_3 reactor with an internal diameter of ca. 20 mm. For the catalytic experiments with this material in the absence of oxygen, 0.17 cm³ (STP) s⁻¹ of pure methane was fed to the reactor containing 10.0 g BaO_2 .

RESULTS AND DISCUSSION

Effect of BaCO_3 content

The effect of BaCO_3 content was studied using catalysts prepared by wet mixing. XRD measurements showed that the calcined materials consisted of separate phases of BaCO_3 and $\text{Ca}(\text{OH})_2$. Upon exposure to atmosphere, CaO strongly adsorbs water to form $\text{Ca}(\text{OH})_2$. Under reaction conditions, the cal-

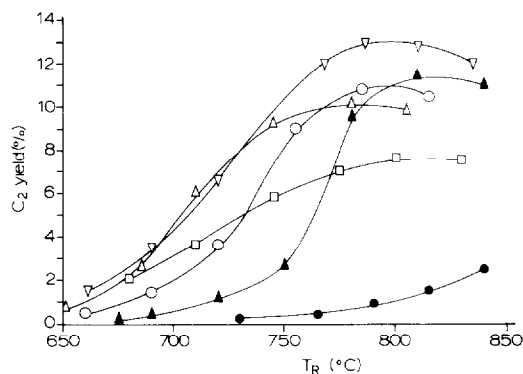


Fig. 2. The effect of BaCO_3 content on the C_2 yield as a function of the reaction temperature T_R ; the results for Li/MgO (B) are shown for comparison. (\square) CaO, (\triangle) 20 mol-% BaCO_3 , (\circ) 80 mol-% BaCO_3 , (\blacktriangle) BaCO_3 , (∇) Li/MgO, (\bullet) empty reactor.

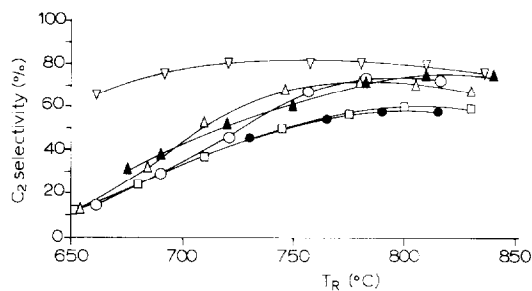


Fig. 3. The effect of BaCO_3 content on the C_2 selectivity as a function of the reaction temperature T_R ; the results for Li/MgO (B) are shown for comparison, Symbols as in Fig. 2.

TABLE 1

Surface areas as a function of the BaCO_3 content for the catalysts of the Ba/CaO series

Catalyst	Area (m^2/g)
$\text{Ca}(\text{OH})_2$	11.8 ± 0.8
20 mol-% BaCO_3	2.0 ± 0.4
60 mol-% BaCO_3	2.5 ± 0.4
80 mol-% BaCO_3	2.3 ± 0.2
BaCO_3	1.7 ± 0.4

cium will probably be present as oxide since $\text{Ca}(\text{OH})_2$ decomposes at ca. 580°C [12].

Fig. 2 shows the C_2 yields as a function of the reaction temperature (T_R) for two Ba/CaO materials and Fig. 3 shows the equivalent selectivities as a func-

tion of T_r . Both figures also give for purposes of comparison the results for pure CaO and BaCO₃ and for Li/MgO (B) [7] obtained under the same conditions. The results obtained for 40 and 60 mol-% BaCO₃ are not given in the two figures as these lie close to those for 80 mol-% BaCO₃. The highest C₂ yield in the Ba/CaO series was reached with pure BaCO₃, at a relatively high temperature of 810°C. Doping CaO with BaCO₃ resulted in a catalyst which was more active at lower reaction temperatures than was the pure BaCO₃. With increasing BaCO₃ content, there was an increase in the temperature at which the optimum C₂ yield was achieved. These maximum C₂ yields are lower than the value obtained with pure BaCO₃ but are still much higher than that found with CaO. The highest C₂ yields and C₂ selectivities shown in Figs. 2 and 3 were reached with the Li/MgO (B) sample. At high temperatures (> 800°C), the selectivities of the Ba/CaO samples were close to those of the Li/MgO (B) sample; however, at lower temperatures, they were significantly lower.

Table 1 shows the surface areas of the samples as a function of the BaCO₃ content. The surface areas of the Ba/CaO materials were, within the experimental error, the same (except for CaO) and are thus not related to the BaCO₃ content. However the surface areas of the catalyst were reduced with respect to that of CaO on addition of BaCO₃ and this reduction in surface area may have given rise to a reduction in the degree of deep oxidation to carbon monoxide and carbon dioxide [13]. It is concluded that the differences in the catalytic behaviour of the Ba/CaO catalysts, except for that of CaO, cannot be attributed to changes in surface area.

By analogy with the Li/MgO system [7], it is possible that the active site on the Ba/CaO catalyst is associated with the decomposition of surface carbonate species. In order to test this idea, TPD measurements were carried out to examine the ease of decomposition of the carbonate phases; results for the

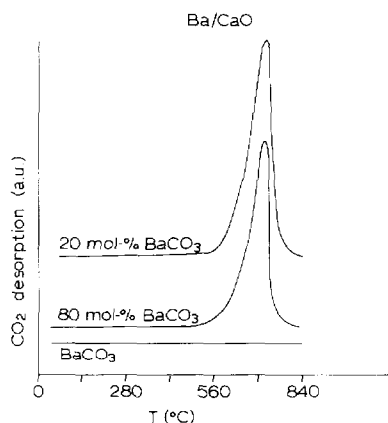


Fig. 4. The rate of desorption of carbon dioxide from Ba/CaO catalysts as a function of temperature.

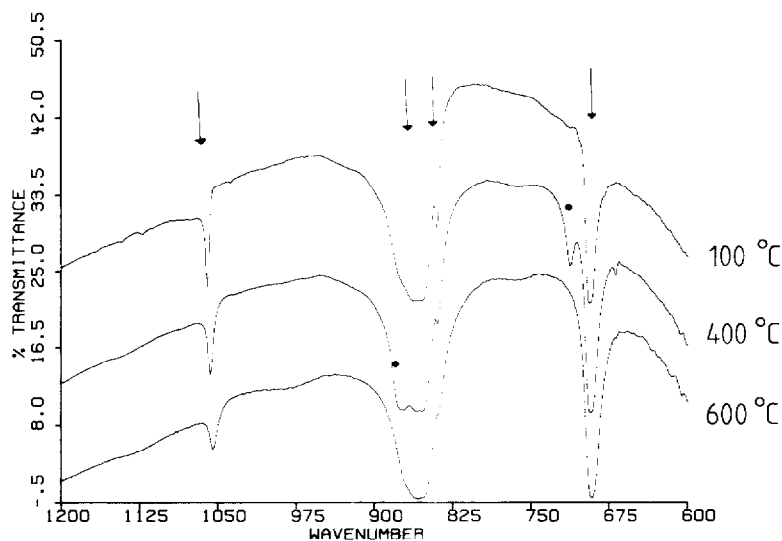


Fig. 5. FTIR spectra of Ba/CaO samples as a function of temperature of treatment.

production of carbon dioxide from the decomposition of the carbonate phase are given in Fig. 4. The results for 40 and 60 mol-% BaCO₃ samples, again not shown, were analogous to those for the 20 and 80 mol-% samples. The desorption of carbon dioxide begins at around 540 °C for all the Ba/CaO samples and is complete at about 840 °C. However, as is also shown in Fig. 4, there was no decomposition of the pure BaCO₃ material in the measured range of temperatures up to 840 °C. In order to try to explain why BaCO₃ combined with CaO apparently decomposes at lower temperatures, FTIR spectra were obtained with the Ba/CaO samples as a function of temperature of treatment. Typical results for the 20 mol-% sample are shown in Fig. 5. After drying in technical air at 100 °C, the sample showed typical bands from BaCO₃: at 696 cm⁻¹, 839 cm⁻¹, 858 cm⁻¹ and 1055 cm⁻¹, shown in the figure by (↓). After calcination at 400 °C, two bands typical of CaCO₃ appeared at 710 cm⁻¹ and 872 cm⁻¹, shown in the figure by (•). However, these CaCO₃ bands disappeared after calcination at 600 °C. Comparison of these results with the TPD data of Fig. 4 showed that this was consistent with the desorption of carbon dioxide starting at around 540 °C. Fig. 5 also shows that only a part of the BaCO₃ had decomposed. It would thus appear that the partial decomposition of BaCO₃ occurs by way of the formation of CaCO₃ as an intermediate. The CaCO₃ was not present in the freshly prepared sample.

Oxidative coupling of methane over BaO₂

It has been suggested in the literature [5] that the active oxygen species responsible for the activation of methane is diatomic. We have previously stud-

ied the rate of reaction of methane with oxygen in the presence of a Li/MgO catalyst as a function of the partial pressures of methane, oxygen and carbon dioxide [14] and concluded that the rate determining step involves reaction of methane adsorbed on the catalyst surface with a relatively weakly adsorbed diatomic oxygen species. In this section, we describe the reaction between methane and the peroxide anion O_2^{2-} of BaO_2 in order to obtain more information about the active site.

A sample of 10.0 g of BaO_2 was placed in the reactor and was first treated in a stream of oxygen (0.5 h) and then helium (0.5 h) at $470^\circ C$. A stream of methane ($0.17\text{ cm}^3(\text{STP})\text{s}^{-1}$) was then fed to the reactor at $T_R=470^\circ C$. The initial C_2 yield was 1.50%, the reaction appearing to have 100% selectivity to ethane (based on the measured concentrations of the products). After 2 h, the C_2 yield was 0.63%, the apparent selectivity to ethane being the same. The absence of carbon monoxide and carbon dioxide in the gas phase indicates that if these compounds are formed, they are captured by BaO_2 to form $BaCO_3$. Analysis showed that the carbon dioxide content of the catalyst after use was higher than that before use. Analogous results have been reported by Otsuka et al. [15]. Sinev et al. [16] also found a selectivity of 100% to ethane when pulses of methane in a helium stream were injected over a BaO_2 sample. However, they did not consider the possibility of the formation of $BaCO_3$.

Since the oxidative coupling of methane usually requires temperatures higher than about $600^\circ C$ [1-7], these results show that BaO_2 is capable of breaking the C-H bonds in methane and of forming C_2 products at lower temperatures. We thus conclude that O_2^{2-} may be the active oxygen species in the methane coupling reaction over the barium doped material. A tentative explanation for the higher reaction temperature of methane with Ba/CaO when compared with the reaction temperature of methane with BaO_2 is that in the former case the peroxide species are more isolated on the surface of the catalyst resulting in an overall retardation of reaction.

Effect of helium pretreatment

It was found that when a Ba/CaO catalyst was pretreated in the reactor in helium for 3 h at $800^\circ C$, the initial apparent C_2 selectivity was much higher than in the case of a sample which had not been pretreated; however, the C_2 yield was the same. The in-situ pretreatment in helium at a temperature high enough to bring about the decomposition of the carbonate was thus not detrimental to the activity of the catalyst; such a pretreatment was previously shown to be detrimental for Li/MgO catalysts [17]. When the used Ba/CaO sample was measured in the TPD equipment, a desorption profile analogue to those for fresh Ba/CaO samples (Fig. 4) was found. It would thus appear that the carbonate reforms, at least partially, during reaction; the carbon dioxide formed

in the initial stages of reaction does not appear in the gas phase and so the C_2 selectivity is higher.

Stability of Ba/CaO catalysts

Fig. 6 shows the C_2 yields of one of the Ba/CaO materials, 20 mol-% $BaCO_3$, as a function of time-on-stream in (a) a quartz and (b) a fused Al_2O_3 reactor at $T_R = 800^\circ C$. For purposes of comparison, the results of equivalent experiments for Li/MgO (B) in both types of reactor, as well as those for a K/MgO (1 mol-% K_2CO_3) catalyst in a quartz reactor, are also given. Table 2 shows the C_2 yield and the C_2 selectivity of each of these catalysts after different times on stream; it also shows the contents (mol-%) of the dopants before and after use in each case. The results in each type of reactor will now be discussed in turn.

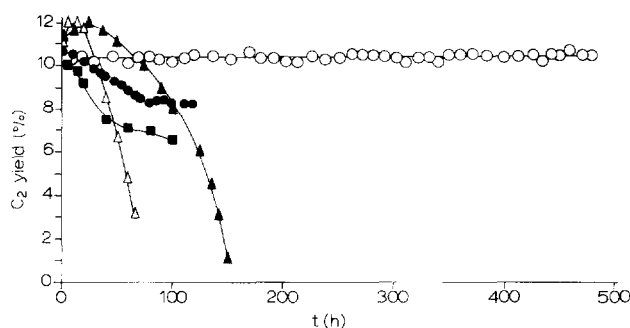


Fig. 6. The C_2 yield as a function of time-on-stream at $T_R = 800^\circ C$ for (○) Ba/CaO, Al_2O_3 ; (●) Ba/CaO, quartz; (▲) Li/MgO (B), Al_2O_3 ; (△) Li/MgO (B), quartz; (■) K/MgO, quartz.

TABLE 2

Results for Ba/CaO at various times of use compared with equivalent data for Li/MgO (B) and K/MgO, $T_R = 800^\circ C$

Catalyst	Reactor	mol-% dopant		C_2 yield			C_2 selectivity		
		Fresh	Used	5 h	60 h	100 h	5 h	60 h	100 h
Li/MgO (B)	quartz	10.0	0.6	12.2	4.8	—	83	83	—
Li/MgO (B)	Al_2O_3	10.0	0.4	11.2	10.6	8.0	82	83	82
K/MgO	quartz	1.0	0.05	10.6	6.9	5.9	69	58	55
Ba/CaO	quartz	20.0	20.9	10.6	8.9	8.2	71	69	64
Ba/CaO	Al_2O_3	20	20.8	10.3	10.2	10.2	71	70	71

Quartz reactor

Fig. 6 and Table 2 show that the Li/MgO and K/MgO samples deactivated relatively rapidly. This is apparently caused by the loss of the dopant by the formation of the corresponding meta-silicate and the formation of the volatile hydroxide, as discussed previously [7]. The Ba/CaO sample showed a more stable behaviour but also deactivated slowly. In the case of the K/MgO and Ba/CaO samples, there was a decrease in C₂ selectivity during deactivation. The drop in selectivity and activity of the latter sample appears to have been due to the deposition of silicon-containing species on the surface of the catalyst sample during use: XRF measurements showed the presence of silicon, probably as SiO₂, in the used samples. Furthermore, when XRF analyses were carried out with powdered samples straight out of the reactor, a higher concentration of silica was found than when they were carried out with fused samples of the same material; as the surface area of the former was greater, this indicates that the silicon was probably concentrated at the surface.

Fused Al₂O₃ reactor

In a fused Al₂O₃ reactor, the deactivation of the Li/MgO (B) catalyst was much slower than for the same sample in the SiO₂ reactor. This (residual) deactivation is likely to have been due mainly to the formation and consequent loss of the volatile LiOH. In contrast, the Ba/CaO catalyst did not deactivate, even after 480 h on stream (Fig. 6).

Effect of the residence time

In an attempt to understand the reaction pathways leading to both the partial and the complete oxidation of methane, the effect of varying the residence time (W/F) was studied holding the flow-rate F constant at 1.67 cm³ (STP) s⁻¹ and varying the catalyst weight, W ; this was done for both a Ba/CaO sample (20 mol-% BaCO₃) and for the Li/MgO (B) material. In a previous paper [18], we showed, using Li/MgO, that back-mixing of the reaction mixture had a negative effect on the C₂ selectivity: as ethane and ethylene are susceptible to oxidation, the optimum selectivity is reached under plug-flow conditions. When a flow-rate F of 1.67 cm³ (STP) s⁻¹ is used, the reactor can thus be considered to be operating under plug flow conditions [18]. Furthermore, reactions occurring in the so-called "post-catalytic volume" (deep oxidation of the C₂ products) are negligible with this rate of gas flow [11]. As a consequence, experiments in which W rather than F is varied allow the effect of residence time to be examined without the results being effected by these factors. This point will be discussed in more detail at the end of this section.

Ba/CaO

Fig. 7 shows how the product selectivity, the oxygen conversion and the C_2 yield vary as a function of W/F (proportional to the residence time) at $T_R = 710^\circ\text{C}$. There was no reaction in the empty reactor at this temperature. The C_2 yield and C_2 selectivity both increased with increase in residence time; similarly, both the ethane and ethylene selectivity increased with W/F . At low residence times, no ethylene was formed, showing that ethylene is not a primary product. The carbon monoxide selectivity was high at low residence times and there was a strong decline in carbon monoxide selectivity and a small increase in carbon dioxide selectivity with increasing residence time. Analogous results were found for La_2O_3 at 670°C and for $\text{Na}/\text{Sm}_2\text{O}_3$ at 710°C [19].

The results for the same sample at 800°C , shown in Fig. 8, were different to those at the lower temperature of 710°C . The selectivity to ethane and the total C_2 selectivity were both much higher at low residence times and did not change so much with W/F . There was an increase in the C_2 yield and C_2 selectivity with an increase in residence time but the C_2 selectivity remained constant over almost the whole range of W/F (Fig. 8a); however, the ethane selectivity decreased and the ethylene selectivity increased with increasing W/F .

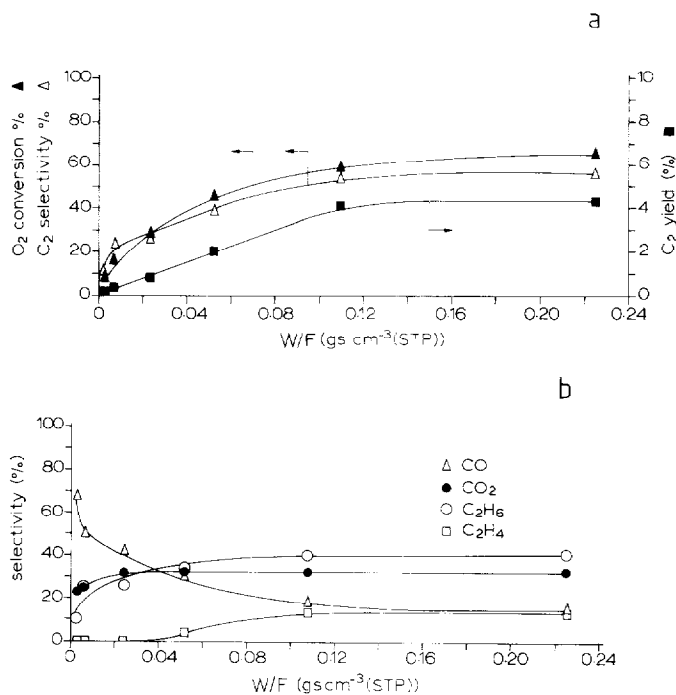
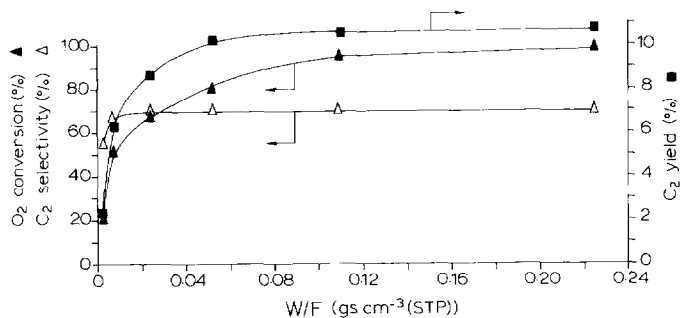


Fig. 7. Oxygen conversion and C_2 yield (a) and product selectivity (b) as a function of W/F at $T_R = 710^\circ\text{C}$ for Ba/CaO (20 mol-% BaCO_3).



b

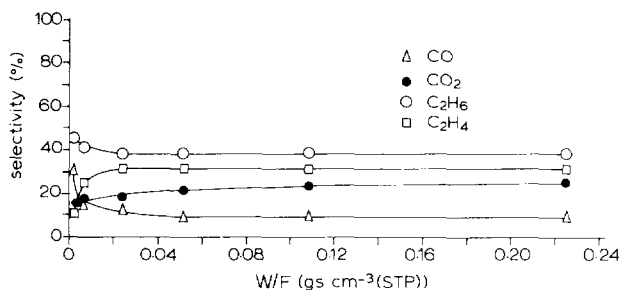


Fig. 8. Oxygen conversion and C_2 yield (a) and product selectivity (b) as a function of W/F at $T_R=800^\circ\text{C}$ for Ba/CaO (20 mol-% BaCO_3).

F at low values of W/F , both reaching constant values at higher W/F (Fig. 8b).

Li/MgO

Fig. 9 shows equivalent results to those of Fig. 7 for Li/MgO (B) at $T_R=710^\circ\text{C}$. Only ethane and carbon dioxide were formed at low residence times, the selectivity to ethane being high; these results show that carbon monoxide and ethylene are not primary products with this catalyst under these conditions. There was a small increase in C_2 selectivity with increasing residence time at low values while the C_2 yield increased over the whole range of W/F as a result of increasing conversions. The carbon dioxide selectivity decreased with increasing residence times and a small amount of carbon monoxide was formed. Fig. 10 shows equivalent results for the effect of residence time at the higher temperature of 780°C for the Li/MgO (B) sample. The selectivity to ethane was again very high at low residence times (Fig. 9b) but it decreased markedly and the ethylene selectivity increased with increasing W/F ; the carbon monoxide selectivity decreased with increasing residence time while the carbon dioxide selectivity first decreased slightly and then increased. The C_2 selectivity was virtually constant for all values of the residence time.

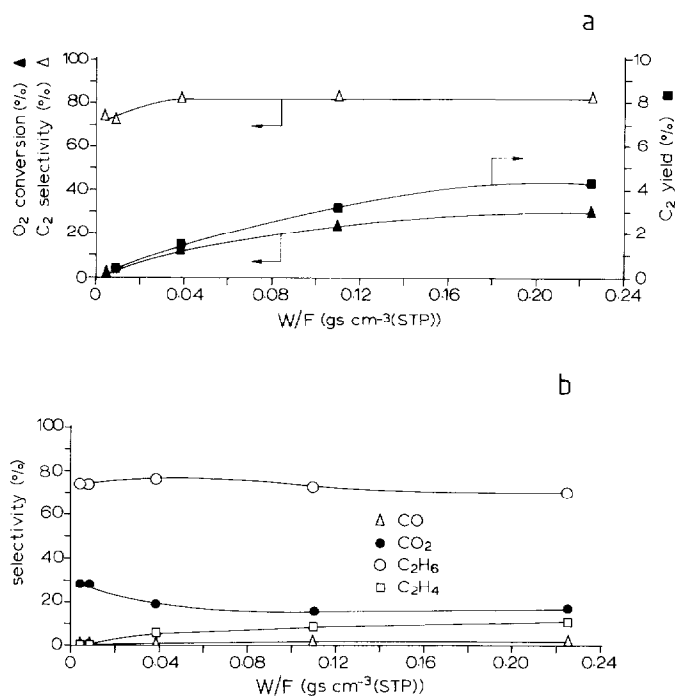


Fig. 9. Oxygen conversion and C_2 yield (a) and product selectivity (b) as a function of W/F at $T_R = 710^\circ\text{C}$ for Li/MgO (B).

Initial rates

Fig. 11 shows the product concentrations (mol-%) as a function of W/F for Ba/CaO at $T_R = 710^\circ\text{C}$ and Fig. 12 shows equivalent results to those of Fig. 11 for Li/MgO (B). The initial rates for Ba/CaO and Li/MgO (B) at 710°C can be calculated from these figures. Table 3 compares the initial rates for both catalysts; in order to calculate the rates, it was assumed that the bulk density of each of the catalysts was 1 g/cm^3 . The rate of reaction to form ethane was of the same order of magnitude for each type of catalyst. However the rate of CO_x production for the Ba/CaO catalyst was much higher, this resulting in a relatively low selectivity to ethane. Table 3 also shows that ethylene is not a primary product ($R_{\text{C}_2\text{H}_4} = 0$), for both catalysts. The calculated selectivities obtained from the initial rates are in good agreement with the (extrapolated) selectivities at $W/F=0$ given in Figs. 7 and 9.

Significance of these results for the reaction sequence

It is generally argued for the methane coupling reaction that ethane is produced by combination of two CH_3 radicals, formed in the rate determining step; the combination probably occurs at or in the gas phase near the surface [6]:



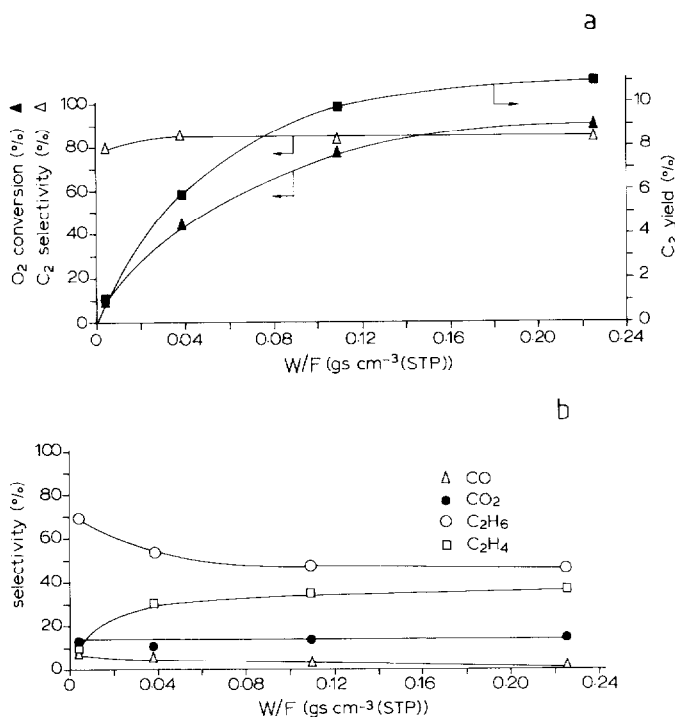


Fig. 10. Oxygen conversion and C_2 yield (a) and product selectivity (b) as a function of W/F at $T_R = 780^\circ\text{C}$ for Li/MgO (B).

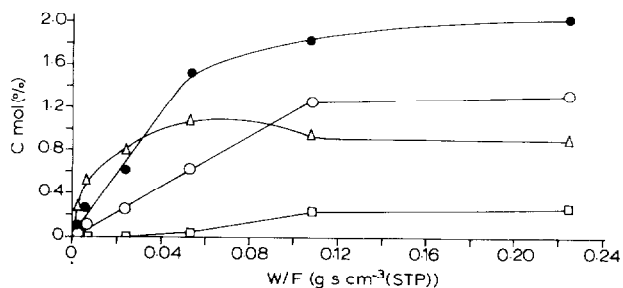


Fig. 11. The product concentrations (mol-%) as a function of W/F for Ba/CaO (20 mol-% BaCO_3) at 710°C . (Δ) Carbon monoxide, (\bullet) carbon dioxide, (\circ) ethane, (\square) ethylene.

According to reaction (1), the rate of formation of the C_2 compounds should be proportional to the square of the CH_3 concentration; if one assumed that carbon monoxide and carbon dioxide are formed from single CH_3 species, one can conclude that the rate of formation of these species will have a lower order with respect to the CH_3 concentration [6]. An increase in the amount of catalyst, W , (keeping F constant) and an increase in temperature will both give rise to the production of more methyl radicals; this in turn will thus favour the

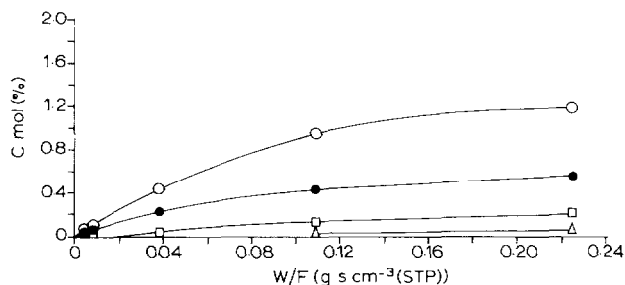


Fig. 12. The product concentrations (mol-%) as a function of W/F for Li/MgO (B) at 710°C . Symbols as in Fig. 11.

TABLE 3

The initial rates and initial selectivities for Ba/CaO (20 mol-% BaCO_3) and Li/MgO (B) at 710°C

Product	Initial rate ($10^{-5} \text{ mol s}^{-1}$)	Initial selectivity
<i>Ba/CaO</i>		
C_2H_6	1.67	11.9
C_2H_4	0	0
CO	10.41	74.3
CO_2	1.94	13.8
<i>Li/MgO</i>		
C_2H_6	1.54	75.5
C_2H_4	0	0
CO	0	0
CO_2	0.50	24.5

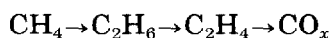
formation of C_2 products. This increased formation of C_2 species will only be appreciable if further oxidation of the C_2 products to carbon monoxide and carbon dioxide is relatively insignificant. The results given in Figs. 7–10 indeed show that increases in W/F (with F constant) or temperature result in an increase in C_2 selectivity and C_2 yield for both types of catalyst studied.

For the Ba/CaO system, the C_2 selectivities at low W/F are very low at $T_R = 710^{\circ}\text{C}$ (Fig. 7). We thus conclude that the methyl radicals which are formed can also easily be oxidized. (This also applies to the La_2O_3 and Na/ Sm_2O_3 catalyst systems [19]). However, the results for Li/MgO at $T_R = 710^{\circ}\text{C}$ (Fig. 9) are very different, high C_2 selectivities being found at low W/F . We thus conclude that the direct oxidation of the methyl radicals to give carbon monoxide and carbon dioxide plays a much smaller role over Li/MgO than over Ba/CaO.

It is reasonably widely agreed that ethane is a primary product of methane

activation and that ethylene is formed by (oxidative) dehydrogenation of ethane [1-7]. That conversion of ethane into ethylene occurs at the high reaction temperatures for both catalyst systems is seen clearly in Figs. 8b and 10b. For Ba/CaO at $T_R=800^\circ\text{C}$ and Li/MgO at $T_R=780^\circ\text{C}$, it might be expected that there would, at higher residence times, be an increase in the selectivity to carbon monoxide and carbon dioxide as a result of the deep oxidation of the C_2 products. However, as shown in Figs. 8 and 10, this is not the case, probably because of the very high oxygen conversions: the oxygen concentrations at the end of the catalyst bed will thus be very low and sequential reaction will thus be minimised.

We have recently suggested in a series of papers [9,18,20] that the oxides of carbon are formed predominantly from the C_2 products over Li/MgO catalysts. The sequential oxidation becomes more important with increasing temperature, increasing oxygen partial pressure and increasing partial pressures of ethane and ethylene. Using a continuous stirred tank reactor (CSTR) [9], we have shown that the reactions taking place during the oxidative coupling of methane over Li/MgO at 720°C occur predominantly as follows:



Under the conditions of the CSTR (high $W/F=3.76 \text{ g s cm}^{-3}$ (STP)), a high concentration of CH_3 radicals and thus high concentrations of ethane and ethylene are formed; hence, the formation of CO_x from the C_2 products will also be very significant. Thus, under the conditions of the CSTR, the rate of oxidation of the methyl radicals and the oxidation of ethane will be negligible in relation to the rate of oxidation of ethylene.

Effect of gas flow

A number of investigations have in the past been carried out on the CH_4/O_2 system to study the effect of residence time on the behaviour of catalyst systems by varying the gas flow through the reactor [4, 21-23]. In contrast to our results for Li/MgO, Edwards and Tyler [21] and Hutchings et al. [22] found a decrease in C_2 selectivity with increasing W/F for the same catalyst system; in both cases, W was kept constant and F decreased. Asami et al. [4] in their work on PbO/MgO, also varied the flow, but found a small increase in C_2 selectivity with increasing W/F . The dependence of the product selectivity upon residence time found for Sr/La₂O₃ by Deboy and Hicks [23], who also varied F , showed a very similar behaviour to the results given in this paper for Ba/CaO and also to those to be reported elsewhere for La₂O₃ [19].

Experiments in which the value of W/F is increased by decreasing the gas flow can result in a change of the flow pattern through the reactor, from plug flow at high values of F to ideal mixing behaviour at low values of F [18]. As back-mixing of C_2 products leads to a greater chance of deep oxidation, a decrease in C_2 selectivity will be found when F is decreased while W is kept con-

stant: this is due to a relatively larger effect of back-mixing by diffusion (in a direction opposite to the gas flow) at lower flow-rates. The results for Li/MgO, obtained by Edwards and Tyler [21] and by Hutchings et al. [22] are probably influenced by this effect and are thus not only an effect of residence time. We therefore firmly believe that residence time measurements should be carried out under plug flow conditions.

It could be argued that measurements at low values of W could be influenced by channeling [18]. This was probably not the case in our measurements as the same catalytic results were obtained when the flow was increased by a factor 2 while W/F was kept constant.

Inhibition of total oxidation

It has been reported in the literature that the oxidation of hydrocarbons in a flame is retarded by injecting alkali carbonates, e.g. finely powdered Na_2CO_3 , into the flame [24–26]. The flame retarding effect of the alkali carbonates has been explained in two ways: (i) *thermal inhibition*: the decomposition of Na_2CO_3 absorbs heat from the flame, thus lowering reaction rates; (ii) *chemical inhibition*: volatile alkali hydroxides are believed to be formed from the carbonates, reacting with a hydrogen radical (a very reactive chain carrier) to form the alkali metal and water [24–26]. The alkali hydroxide is reformed by the reaction of the alkali metal with an (also very reactive) OH radical. The rate of oxidation is thus lowered by the removal of active chain carriers.

Table 4 compares the conversions, selectivities and yields given by a sample of 0.01 g Ba/CaO (20 mol-% BaCO_3) at 710°C with equivalent results obtained with a physical mixture of 0.01 g Ba/CaO and 0.300 g Na_2CO_3 ; at this temperature, Na_2CO_3 by itself was found to be inactive in the methane coupling reaction. It can be seen that the addition of Na_2CO_3 improved the C_2 selectivity and the C_2 yield while the oxygen conversion stayed the same. It is thus concluded that the rate of total oxidation (with contributions from the oxidation of methyl radicals, ethane and ethylene) is lowered by the presence of the Na_2CO_3 . Li_2CO_3 almost certainly has the same effect but could not be used for this type of physical mixing experiment because it melts at this tem-

TABLE 4

The inhibition of total oxidation by Na_2CO_3 $T_R = 710^\circ\text{C}$

Catalyst	Conversion (%)		Selectivities (%)				S_2 (%)	Y_2 (%)
	CH_4	O_2	C_2H_6	C_2H_4	CO_2	CO		
Ba/CaO	1.54	16	23.5	—	25.5	51.0	23.5	0.36
Ba/CaO + Na_2CO_3	2.17	15	41.1	1.3	28.1	29.5	42.4	0.92

perature. The first explanation of the flame retarding effect of alkali carbonates given above, the thermal (heat sink) effect, is not applicable to this experiment as the temperature in the reactor was kept constant by the oven. The second, explanation is therefore favoured: the alkali carbonates are volatilised and reduce the number of chain carriers of the oxidation reaction. We have shown elsewhere that the addition of Na_2CO_3 and K_2CO_3 lowers the total oxidation rate of ethane and ethylene in an otherwise empty reactor [9].

We therefore conclude that a good catalyst used in the oxidative coupling of methane has two functions: (1) the production of CH_3 radicals; and (2) the inhibition of both the total oxidation of these radicals and the total oxidation of ethane and ethylene. In the comparative catalytic studies which we have carried out to date, the highest C_2 selectivities have been reached with catalysts containing Li_2CO_3 or Na_2CO_3 (e.g. Li/MgO , Li/CaO , Na/CaO , $\text{Na/Sm}_2\text{O}_3$). It was shown that LiOH and NaOH are easily formed under reaction conditions and that the loss of these volatile alkali hydroxides causes deactivation of these catalysts; the formation of LiOH and NaOH also explains the very high selectivities of these catalysts: the volatile hydroxides lower the oxidation of methyl radicals and the oxidation of ethane and ethylene. These two explanations seem to be contradictory, but this is not the case since we have shown that only small amounts of lithium are needed to create the necessary sites on the surface of the Li/MgO catalyst [17] and since we have also shown that the C_2 selectivity remains virtually constant during deactivation of the Li/MgO catalyst. BaCO_3 cannot be volatilised under the reaction conditions of methane coupling and so the Ba/CaO catalysts have high stability; however, the C_2 selectivity is lower than that of Li/MgO due to the higher rate of oxidation of CH_3 radicals and C_2 products. The mobile Li_2CO_3 on the surface of the Li/MgO catalyst can possibly also inhibit the oxidation of methyl radicals and C_2 products to CO_x [27,28], resulting in the higher C_2 selectivity when compared with Ba/CaO .

CONCLUSIONS

1. Doping CaO with BaCO_3 results in a catalyst which is more active at lower reaction temperatures than is BaCO_3 . The active site in the case of Ba/CaO is probably formed by the partial decomposition of the BaCO_3 via the formation and subsequent decomposition of CaCO_3 .

2. BaO_2 is very active in breaking the C-H bonds of methane and in the formation of C_2 products. The active oxygen entity in the case of Ba/CaO is probably an O_2^{2-} species.

3. Ba/CaO is more stable but less selective than is Li/MgO . The loss of lithium by the formation of LiOH explains the deactivation of Li/MgO but also explains the very high selectivity of this catalyst; the volatile hydroxide lowers the oxidation of methyl radicals, ethane and ethylene.

4. The direct oxidation of methyl radicals to given carbon monoxide and carbon dioxide plays a more important role in the case of Ba/CaO than in that of Li/MgO.

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