

The Selective Oxidation of Methane to Ethane and Ethylene over Doped and Un-doped Rare Earth Oxides

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ABSTRACT

A comparison has been made of the behaviour in the oxidative coupling of methane of the oxides of Sm, Dy, Gd, La and Tb with that of a Li/MgO material. All but the Tb₄O₇ (which gave total oxidation) were found to give higher yields than the Li/MgO material at temperatures up to approaching 750°C but the Li/MgO system gave better results at higher temperatures. The cubic structure of Sm₂O₃ was found to be responsible for its good performance while the monoclinic structure was relatively inactive and unselective. The addition of Na or Ca to cubic Sm₂O₃ gives a higher optimum C₂ yield than that of unpromoted Sm₂O₃. Sm₂O₃ and Ca/Sm₂O₃ catalysts are more stable than Li/MgO, Li/Sm₂O₃ or Na/Sm₂O₃. The addition of Li or Na to Sm₂O₃ causes the structure to change from cubic to monoclinic; the deactivation of the Na/Sm₂O₃ catalysts is caused by a loss of Na coupled with the formation of the monoclinic form of Sm₂O₃.

INTRODUCTION

The oxidative coupling of methane (the principal constituent of natural gas) to give a mixture of ethane and ethylene is a potentially important process; if the yield of the reaction (conversion x selectivity) is high enough, the reaction could compete with indirect routes using synthesis gas. However, because of the high stability of the methane molecule, such a conversion requires active catalysts which do not give total oxidation. A large research effort is currently being directed towards finding such catalysts and towards understanding the mechanism of the reaction [1-10].

Good catalysts for the oxidative coupling of methane under continuous flow conditions (as opposed to cyclic operation conditions) have to satisfy three requirements:

- (i) They should possess suitable surface sites. In the case of Sm₂O₃, for example, surface O₂⁻ or O₂²⁻ species are believed to be the active oxygen entities [3].
- (ii) The catalysts should be solid bases. According to Bytyn and Baerns [4], catalysts with acidic sites easily form CH₅⁺ species; these species are unstable and give rise to the formation of CO₂.

(iii) The ability of the catalyst to supply oxygen should be limited. Catalysts which have ions of variable valency have poor selectivity for the oxidative coupling of methane [5].

Otsuka and his coworkers [3,6,7] have investigated the methane coupling reaction over the oxides of the rare earths. Their best results were obtained with Sm_2O_3 and Dy_2O_3 : each gave a selectivity of 93%. However, the reactor feed used in their investigation was very dilute (82% He; total pressure 1 atm.) and the CH_4/O_2 ratio used (46:1) resulted in a low conversion of methane (ca. 4%).

We have previously reported [5,8,9] on a number of aspects of the methane coupling reaction using various different types of catalysts, particularly $\text{PbO}/\text{Al}_2\text{O}_3$ and $\text{Li}_2\text{CO}_3/\text{MgO}$, paying particular attention to the nature of the active phase, the effect of reaction conditions and the ageing behaviour of the catalysts. In this paper we present results, obtained using more concentrated gas feeds with lower CH_4/O_2 ratios than those used by Otsuka et al. [3,6,7], these allowing a comparison of the activities and selectivities of some rare earth oxides with those of the $\text{Li}_2\text{CO}_3/\text{MgO}$ system. Having shown that Sm_2O_3 is one of the most promising materials under our conditions, we examine the effect of various dopants (Li, Na and Ca) on the behaviour of Sm_2O_3 . We show that an important feature of the use of such materials is the stabilisation of the Sm_2O_3 in the cubic phase. The $\text{CaO}/\text{Sm}_2\text{O}_3$ system appears to be particularly promising, showing little sign of deactivation during use.

EXPERIMENTAL

Catalyst Preparation

The rare earth oxide catalysts were standard commercial samples of the oxides (Serva) and were calcined in air at 850°C for 1h prior to use. The doped Sm_2O_3 materials were prepared by wet impregnation of Sm_2O_3 (in powder form) with an aqueous solution of the desired nitrate. After drying at 140°C , the impregnated samples were also calcined in air at $T_c = 850^\circ\text{C}$ (6h). The preparation of the $\text{Li}_2\text{CO}_3/\text{MgO}$ sample used for comparison purposes ("Li/MgO (B)") has been described previously [9]. All the calcined materials had a granular form and were thus crushed and sieved to a particle size of 0.3-0.6mm before use.

Catalytic Experiments

The catalytic experiments were carried out in a quartz fixed-bed reactor operated at a pressure of one atmosphere. Two types of reactor were used: reactor 1 had a heated volume of about 20 cm^3 after the catalyst bed and reactor 2 had a much smaller post-catalytic volume of about 3 cm^3 . The

internal diameter of both types of reactor was 4 mm. The gas feed consisted of methane and air which were admitted separately using mass-flow controllers and were pre-mixed before entering the reactor. The experiments reported here were carried out with a methane/oxygen ratio of either 5:1 or 10:1. All gas analyses were performed by gas chromatography as described previously [8]. In the experiments using reactor 2, two sets of reaction conditions were used, each with the same contact time in the catalyst bed: (i) a low superficial gas velocity, with a catalyst weight, W , of 0.093 g and a gas flow rate, F , of $0.42 \text{ cm}^3(\text{STP})\text{s}^{-1}$; and (ii) a high specific gas velocity, with $W = 0.744 \text{ g}$ and $F = 3.33 \text{ cm}^3(\text{STP})\text{s}^{-1}$. Unless otherwise stated, the low gas velocity conditions were used and this was also the case for reactor 1.

Catalyst Analysis and Characterization

Atomic absorption spectroscopy (AAS) was used to determine the weight percentages of Li, Na and Ca in the catalysts before and after use. X-ray powder diffraction was carried out with a Philips PW 1050 diffractometer using $\text{Cu-K}\alpha$ radiation. Surface areas were determined by the BET method using Ar adsorption. The extent of adsorption of CO_2 on Sm_2O_3 was used as a measure of the number of basic sites on the catalyst. The extent of adsorption was determined, using a flow system equipped with a thermal conductivity cell, from the temperature programmed desorption (TPD) profiles for the desorption of preadsorbed CO_2 , the heating rate being $14^\circ\text{C min}^{-1}$; the profiles were recorded after CO_2 adsorption at ambient temperature on a sample of catalyst pretreated at 800°C for 1h in a He stream.

RESULTS AND DISCUSSION

The Catalytic Behaviour of the Oxides of Sm, Dy, La, Gd, and Tb Comparison with Li/MgO.

The activities and selectivities for the formation of C_2H_6 and C_2H_4 of a series of freshly calcined rare earth oxides, Sm_2O_3 , Dy_2O_3 , La_2O_3 , Gd_2O_3 and Tb_4O_7 , were determined in reactor 1 using a methane/oxygen feed ratio of 10:1. The results of these experiments are given in Figure 1, which shows the yield (conversion x selectivity) of C_2 products as a function of the reaction temperature, T_R . For comparison purposes, Figure 1 also shows results obtained under the same reaction conditions [9] for the lithium-promoted magnesium oxide catalyst (Li/MgO (B)). The results for the rare earth oxides depict a number of unusual features when compared with those for Li/MgO(B). For example, they all show activity at lower temperatures than those found for the Li/MgO sample, each giving appreciable yields at temperatures above about 600°C . All of the rare

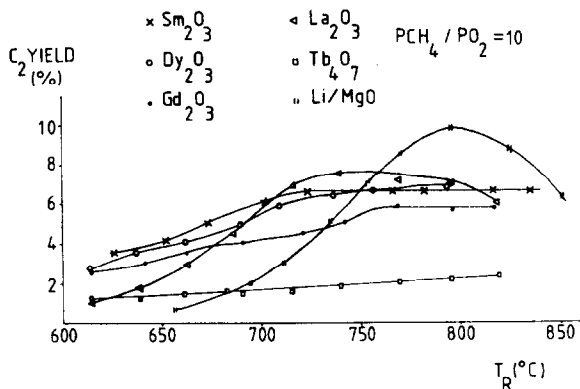


Figure 1 The C_2 yields as a function of T_R of some rare earth oxides compared with those for a Li/MgO catalyst.

earth materials gave 100% conversion of the oxygen in the reaction mixture at all temperatures in the range shown; this contrasts with the Li/MgO catalyst, which only achieved 100% conversion of oxygen at the point at which the maximum yield was achieved (about 800°C). While the selectivity of the Li/MgO catalyst changed little over the whole temperature range examined, the selectivities of the rare earths increased with increasing temperature, this giving rise to the increase in yield; the increase in selectivity also resulted in an increase in conversion of methane, as more oxygen remained available for the selective reaction. Table 1 shows the data for each of the catalysts of Figure 1 at the temperature (T_R) at which the maximum yield was obtained; it also gives the surface area measured for each sample. Most significant of the results shown here is the fact that all the rare earth oxides give lower selectivities than found with the Li/MgO sample; the selectivity for the Tb₄O₇ sample is particularly low, possibly because this material can be partially reduced, a feature which we believe to be associated with increased production of CO₂ [5]. The lower selectivity in this case is in agreement with the results of Otsuka et al. [6].

Although the optimum selectivities of Sm₂O₃, Dy₂O₃ and La₂O₃ (54, 53 and 40% respectively) are much lower than those (of the order of 93%) reported by Otsuka et al. [6], the yields obtained are very much better. This is caused by the very different process conditions used in the two investigations. The C_2 yield of La₂O₃ is relatively high, largely due to a surprisingly high conversion. Lin et al. [10] have shown that the number of

CH₃ radicals generated over La₂O₃ at 500-600°C was much higher than over a sample of Li/MgO containing 7 wt% Li. Since they believed that the same type of centre was responsible for the activation of methane on both types of catalyst, Lin et al. argued qualitatively that the formation of methyl radicals and the overall conversion must parallel one another; this argument thus explains the high conversion of methane obtained on La₂O₃.

The Effect of Post-Catalytic Volume. In the case of the La₂O₃ catalyst, the carbon balance was not 100%; the formation of black carbonaceous deposits was observed in the so-called post-catalytic volume [11] of reactor 1. This is at least partially responsible for the relatively low C₂ selectivity (Table 1). Two important and undesirable reactions can occur in the relatively large heated volume after the catalyst bed : (i) when the oxygen conversion is not 100%, the ethylene formed may react with O₂ to form CO; and (ii) when the oxygen conversion is 100%, the ethylene formed can be cracked to give H₂ and carbon. As the oxygen conversion is 100% throughout the temperature range studied, the latter is probably the case with La₂O₃. To prevent the occurrence of such undesired reactions in the post-catalytic volume, the remainder of the measurements reported here were carried out in reactor 2 in which this volume was much smaller; this gave a small but significant improvement in the selectivities measured.

Table 1 Catalytic results for various rare earth oxides. Reactor 1, PCH₄/PO₂ = 10.

Catalyst	area m ² /g	T _R °C	Conversion(%)		S ₂ (%)	Y ₂ (%)
			CH ₄	O ₂		
Sm ₂ O ₃	9.2	780	12.2	100	54	6.6
Dy ₂ O ₃	6.4	793	12.9	100	53	6.8
Gd ₂ O ₃	12.0	770	12.1	100	48	5.8
La ₂ O ₃	17.0	740	18.8	100	40	7.5
Tb ₄ O ₇	7.7	820	7.8	100	28	2.2
Li/MgO	<1.0	790	12.9	100	75	9.7

The areas given are those determined before use.

Effect of Structural Modification of Sm₂O₃

Because Sm₂O₃ was particularly effective over the whole range of temperatures studied (Figure 1), we decided to concentrate our attention on the properties of this oxide.

Sm₂O₃ can adopt two crystalline structures, cubic and monoclinic [12].

The monoclinic structure is the stable modification while the cubic structure is meta-stable, being that present at temperatures up to about 900°C; at higher temperatures, an irreversible transition into the monoclinic structure takes place. To examine the behaviour of these two modifications, we compared the behaviour of a sample calcined at 850°C (100% cubic) with one calcined at 1000°C (100% monoclinic). Table 2 compares the conversions, selectivities and yields of both structures at $T_R = 780^\circ\text{C}$; the measurements were carried out with a methane/oxygen ratio of 5:1. Detailed product distributions are given in each case. It can be seen that the cubic form is not only more active but that it is also much more selective than the monoclinic sample, the yield of the former modification being almost three times that of the latter.

Table 2 The effect of structure of Sm_2O_3 . $T_R = 780^\circ\text{C}$, $\text{PCH}_4/\text{PO}_2 = 5$.

Catalyst	Conversion(%)		Selectivities(%)				S_2 (%)	Y_2 (%)	area m^2/g
	CH_4	O_2	C_2H_6	C_2H_4	CO_2	CO			
Sm_2O_3 cubic ($T_c = 850^\circ\text{C}$, 6h)	21.9	98	20.2	26.8	40.0	13.0	47.0	10.3	6.6
Sm_2O_3 monoclinic ($T_c = 1000^\circ\text{C}$, 4h)	15.6	94	8.9	16.1	54.6	21.4	25.0	3.9	2.7

The areas given are those determined before use.

The Effect of Basicity and Area of Sm_2O_3 . Using TPD measurements following adsorption of CO_2 , it was shown that the monoclinic modification adsorbed approximately one third of the CO_2 adsorbed by the cubic modification. It was also found that the area of the monoclinic modification was reduced by a factor of approximately 2.4 (Table 2). We thus conclude that the proportion of surface base ($\text{mol CO}_2/\text{m}^2$) is approximately the same for both modifications. Furthermore, the TPD spectrum patterns did not appreciably change from one modification to the other, and we take this to indicate that no substantial change occurred in the nature of the surface basicity.

Catalytic experiments carried out using a higher flow rate, a lower value of W/F and a lower reaction temperature, resulting in a lower O_2 conversion, showed that the specific activity based on the surface area of the cubic phase was much higher than that of the monoclinic phase. These measurements, which will be reported in detail elsewhere [13], together with

the measurements given above, show that neither the overall basicity nor the surface area are major factors in the change in behaviour during the phase transition from cubic to monoclinic. The role of a specific ion such as O_2^{2-} , which is itself highly basic, appears to be more important: during the phase transformation from cubic to monoclinic, the nature of the active sites (perhaps O_2^{2-}) must change, as the selectivity and the rate of C_2 production of the monoclinic modification are much lower than those of the cubic modification [13].

The Addition of Li, Na and Ca to Cubic Sm_2O_3

Catalytic Results. In an attempt to improve the selectivity to C_2 products of the cubic modification of Sm_2O_3 by modifying its surface structure, we prepared doped materials containing Li, Na and Ca by impregnation with solutions of the respective nitrates. Figure 2 compares the behaviour of some of these samples, as a function of the reaction temperature, with that of the undoped Sm_2O_3 sample. The results given in Figure 2 (and Table 3) are typical of those obtained for the different additives at various concentrations; details of the effect of additive concentration will be discussed in more detail elsewhere [14]. Doping with lithium gives a significant decrease of yield at all reaction temperatures; doping with sodium gives a decrease at lower reaction temperatures and a small but significant increase at higher reaction temperatures; and doping with Ca gives a small but significant increase over the whole range of temperatures. Table 3 shows the C_2 yields and selectivities of the different catalysts at the temperatures at which the optimum behaviour was obtained in each case. The addition of Li gave a slight reduction of selectivity while the addition of Na or Ca gave a small increase. There was no significant change in methane conversion.

The Influence of Additives on the Structure of Sm_2O_3 . Otsuka et al. [15] have also examined the effect of alkali dopants on Sm_2O_3 catalysts. They found that Li-doped Sm_2O_3 was the most active and selective for the formation of C_2 compounds, being superior to the undoped Sm_2O_3 , a result which contrasts with those described above. Apart from the difference in gas composition used, the main difference between our experiments and those of Otsuka et al. was the temperature used for the calcination of the catalysts: they calcined their Li/ Sm_2O_3 catalysts at $700^\circ C$ while our samples were calcined at $850^\circ C$. We therefore examined the structures of our Li/ Sm_2O_3 material as a function of calcination temperature to see if this parameter could have an effect. When the lithium-doped material was calcined at $700^\circ C$ (6h), the structure of the Sm_2O_3 was still cubic; however, with a calcination temperature of $775^\circ C$ (6h) and above, the

structure was monoclinic. The lithium was present as distinct monoclinic LiOH and Li_2CO_3 phases in each case. Examination with XRD of the samples doped with Ca and Na which had been calcined at 850°C showed that the Sm_2O_3 was present in the cubic structure in both cases, there also being approximately 10% of the monoclinic phase in the case of Ca; the calcium was found to be present as cubic CaO and the sodium as monoclinic Na_2CO_3 . As discussed above, the undoped material consisted entirely of the cubic structure. From these results, we conclude that the addition of Li to the Sm_2O_3 has a de-stabilising effect on the resultant catalyst and that the poor behaviour of the Li-doped material calcined at 850°C is probably largely due to the presence of the monoclinic modification of the Sm_2O_3 component of the catalysts. No such effects are found with sodium and calcium under these conditions.

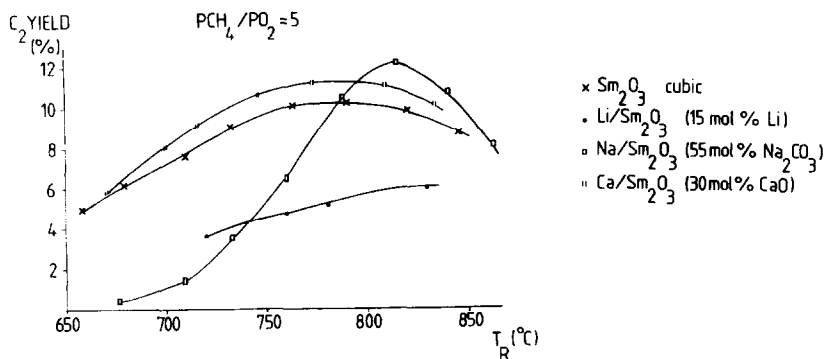


Figure 2 The C_2 yields as a function of T_R of promoted Sm_2O_3 catalysts compared with an unpromoted (cubic) sample.

Table 3 Catalytic results for promoted Sm_2O_3 catalysts compared with an unpromoted (cubic) sample. $\text{PCH}_4/\text{PO}_2 = 5$.

Catalyst	mol%	T_R ($^\circ\text{C}$)	Conversion(%)		Selectivities(%)				S_2 (%)	Y_2 (%)
			CH_4	O_2	C_2H_6	C_2H_4	CO_2	CO		
Sm_2O_3	-	780	21.90	96	20.2	26.8	40.0	13.0	47.0	10.3
$\text{Li}/\text{Sm}_2\text{O}_3$	15	780	14.17	87	11.0	25.0	18.0	46.0	36.0	5.1
$\text{Na}/\text{Sm}_2\text{O}_3$	55	810	21.20	94	25.9	35.1	37.9	5.1	57.0	12.1
$\text{Ca}/\text{Sm}_2\text{O}_3$	30	780	22.60	98	22.6	27.4	42.9	7.1	50.0	11.3

The Effect of Gas Flow

We have shown previously [5,9] for a Li/MgO catalyst that both the conversion and the selectivity are increased considerably if the superficial gas velocity is increased while the contact time is maintained constant. These improvements were thought to be due to better plug-flow behaviour and a consequent reduction of back-mixing in the reactor; a reduction in back-mixing gives a reduction of the degree of further oxidation of the C₂ products to carbon oxides as well as minimising poisoning of the active sites by CO₂ [9]. An increase in gas velocity also results in a decrease in the effects associated with the "post-catalytic volume", as the residence time in this volume is reduced considerably. Similar effects were found for the Na/Sm₂O₃ and Ca/Sm₂O₃ systems and the results are shown in Figures 3a and b; these show respectively the C₂ yields and selectivities as a function of the oven temperatures. In both cases, substantial improvements in yield and selectivity occurred when the superficial gas velocity was increased. The effect was particularly marked for the case of the Ca-doped material, for which the "light-off temperature" decreased by some 100°C and for which very substantial yields were now obtained for an oven temperature of 600°C. A hysteresis effect was observed with the Ca system, the results obtained with reduction of oven temperature being superior to those with increasing oven temperature. This effect seems to arise from the development of hot-spots in the catalyst bed; measurements in which a thermocouple attached to the outside wall of the reactor was moved along the bed to measure temperature profiles [13] showed that a hot-spot of up to 150 - 200°C developed in the case of the Ca/Sm₂O₃ sample and that this remained stationary in one place in the bed during prolonged tests (see below).

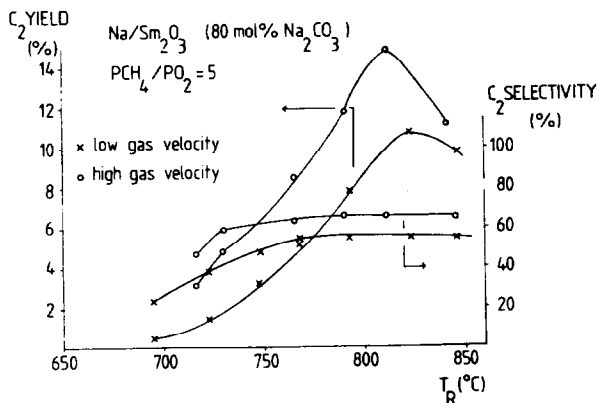


Figure 3a The effect of T_R on the C₂ yield and C₂ selectivity of a Na/Sm₂O₃ catalyst (80 mol% Na₂CO₃) for low (W = 0.093 g, F = 0.42 cm³(STP)s⁻¹) and high (W = 0.750 g, F = 3.33 cm³(STP)s⁻¹) gas velocities.

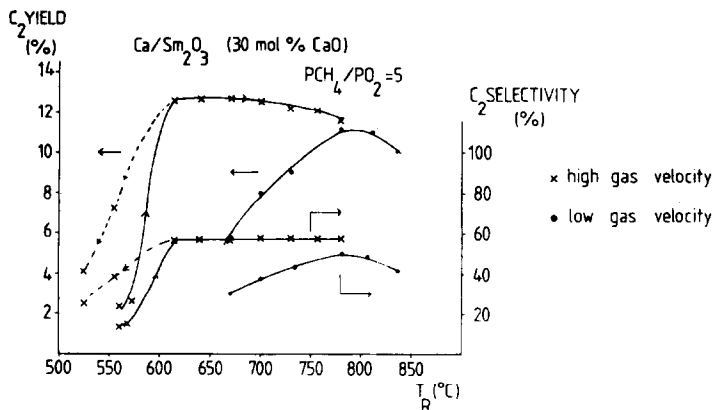


Figure 3b Similar plots to those of Fig. 3a for a CaO/Sm₂O₃ catalyst (30 mol% CaO).

The Stability of Doped Sm₂O₃ Catalysts

Figure 4 shows the C₂ yield as a function of time of reaction under conditions of high superficial gas velocity at the temperature giving the optimum yield for the undoped Sm₂O₃ and the Ca- and Na-doped materials; previously published results [9] for a Li/MgO sample are shown for comparison purposes. The yields and selectivities after 5 and 60 h of operation are shown in Table 4 together with the concentrations (mol%) of the dopant obtained by analysis before and after the experiments. It can be seen that while the Li/MgO sample initially gives a better yield, it loses its advantage over the Sm₂O₃-based materials after some 40 h of operation. The sodium-doped material also disimproves significantly with time while the the unpromoted and calcium-promoted materials exhibit much better behaviour.

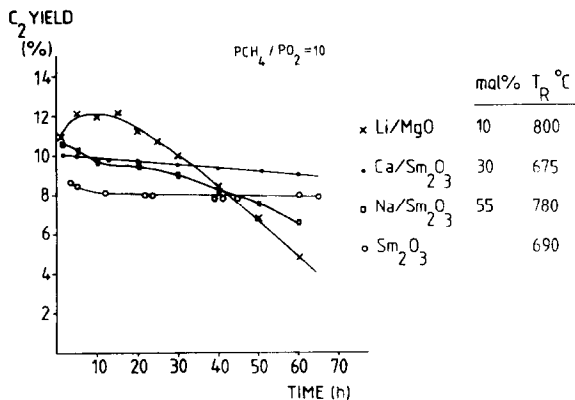


Figure 4 The C₂ yield of undoped and doped Sm₂O₃ catalysts as a function of time compared with data for Li/MgO B [9].

Table 4 The deactivation of undoped and doped Sm_2O_3 catalysts ($T_c = 850^\circ\text{C}$, 6h) compared with data for Li/MgO B [9]. $\text{PCH}_4/\text{PO}_2 = 10$.

Catalyst	mol% dopant		T_R ($^\circ\text{C}$)	C_2 yield		C_2 selectivity	
	Fresh	Used		5h	60h	5h	60h
Sm_2O_3			690	8.4	7.9	60.3	59.6
Ca/ Sm_2O_3	30	30	675	10.0	9.0	70.0	71.0
Na/ Sm_2O_3	55	20	780	10.7	6.4	75.9	65.0
Li/MgO	10	0.6	800	12.2	4.8	83.1	83.2

The initial relatively rapid deactivation (followed by a very slow deactivation) of the unpromoted (cubic) Sm_2O_3 during time on stream at 690°C appeared to have been caused by the formation of coke on the surface of the catalyst: the used catalyst had a grey-black colour and a carbon balance showed a slight loss of carbon from the gas phase during the experiment. During the deactivation, the selectivity remained constant at about 60%, which is consistent with gradual blocking of the active sites without alteration of their character. It was possible to reactivate the catalyst to its original state by treating it in oxygen for 1 h at 690°C . The Sm_2O_3 remained in the cubic modification throughout these experiments.

The deactivation of Ca/ Sm_2O_3 (30 mol% CaO) was also very slow (see Figure 4 and Table 4), occurring over the whole period of use. As with the unpromoted material, the selectivity remained constant throughout; carbon deposition was again observed. There was no loss of calcium during time on stream and Sm_2O_3 remained in the cubic modification. In another experiment at 690°C using a higher oxygen content ($\text{CH}_4/\text{O}_2 = 5:1$), there was no evidence of carbon deposition: a yield of 12.5% with a selectivity to C_2 hydrocarbons of 55% ($\text{C}_2\text{H}_6/\text{C}_2\text{H}_4 = 1.2$) was maintained for 925 h without any change.

The Na/ Sm_2O_3 catalysts deactivated relatively rapidly with a loss of both activity and selectivity; this indicates that there was a change in the nature of the active sites during the experiment. After the experiment, the Na_2CO_3 content of the catalyst (initially 55 mol%) had fallen to ca. 20 mol%. A white deposit, identified as NaOH, was found to have been formed down-stream from the reactor; it was also found that Na had reacted with the quartz reactor to form a Na_2SiO_3 phase. The loss of Na was accompanied by the formation of the monoclinic structure of Sm_2O_3 ; after the experiment, the catalyst was found to contain ca. 50% monoclinic Sm_2O_3 . The transformation of the cubic to the monoclinic Sm_2O_3 is thus associated with the loss of sodium and thus appears to be responsible for the decrease in C_2 selectivity. During the ageing of the catalyst, a hot spot front (with a temperature increase of up to 60°C) was observed to pass through the

catalyst bed. The effect of the movement of the hot spot was examined further by carrying out an equivalent experiment in which the catalyst bed was divided in two parts for examination after the experiment. The results are shown schematically in Figure 5. The lower part of the bed, through which the reaction front had passed, had the pale yellow colour characteristic of monoclinic Sm_2O_3 (which was also shown by XRD) and the Na_2CO_3 content had fallen to 6 mol%. The upper part of the bed still had the cream colour of the cubic modification and the Na_2CO_3 content was 45 mol%. We thus conclude that the sodium was lost by volatilisation at the high temperatures associated with the hot spot. By analogy with the Li/MgO system, in which loss of Li probably occurs by volatilisation of LiOH as well as formation of Li_2SiO_3 [9], we believe that the species which is volatilised is probably NaOH formed during the decomposition of Na_2CO_3 under reaction conditions; it was also found that Na_2SiO_3 had formed on the wall of the reactor.

Figure 4 and Table 4 do not give results for the ageing of a Li/ Sm_2O_3 material as this was found to deactivate very rapidly. The resultant low activity was probably due to the formation of the monoclinic modification which, as discussed above, occurred during calcination, and to the loss of Li; Li_2SiO_3 and the volatile LiOH were formed, the latter being identified on the cooler parts of the reactor above the catalyst bed.

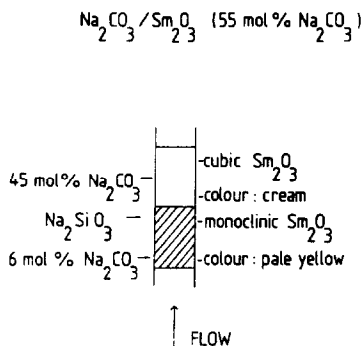


Figure 5 Schematic representation of the reactor after reaction at 780°C for 62 h using a Na/ Sm_2O_3 catalyst (original composition 55 mol% Na_2CO_3).

CONCLUSIONS

1. The oxides of Sm, Dy, Gd and La are more active at low reaction temperature than is Li/MgO. A disadvantage of the use of the rare earth oxides is the low C₂ selectivity compared with that of Li/MgO under the same reaction conditions.
2. The cubic form of Sm₂O₃ is active in methane coupling but the formation of the high-temperature monoclinic form brings about a reduction of C₂ production.
3. The addition of Li caused the structure of Sm₂O₃ to change from cubic to monoclinic, resulting in a poor catalyst for methane coupling.
4. Addition of Na or Ca to cubic Sm₂O₃ gives a higher C₂ yield than that of unpromoted Sm₂O₃.
5. Sm₂O₃ and Ca/Sm₂O₃ catalysts are more stable than Li/MgO but are less selective. Using a methane/oxygen ratio of 10:1, the deactivation is caused by the formation of coke on the surfaces of the catalysts. The use of a higher oxygen concentration in the gas feed prevents the formation of coke and the deactivation.
6. The deactivation of the Na/Sm₂O₃ catalyst is caused by the loss of Na as Na₂SiO₃ or as the volatile species, NaOH, as well as by the formation of monoclinic Sm₂O₃. The loss of Na is coupled with the formation of the monoclinic Sm₂O₃.

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