

An Investigation of the Comparative Reactivities of Ethane and Ethylene in the Presence of Oxygen over Li/MgO and Ca/Sm₂O₃ Catalysts in Relation to the Oxidative Coupling of Methane.

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ABSTRACT

In order to examine the importance of the further oxidation of the desired C₂ products in the oxidative coupling of methane, ethylene and ethane have been added to the feed (containing methane and oxygen) to a Li/MgO or Ca/Sm₂O₃ catalyst. The results of these measurements show that neither of these C₂ molecules is stable under these conditions with either of the catalysts. Additionally, the rates of the oxidation of ethane and of ethylene alone have been measured using a gradientless reactor for both catalysts as well as for a quartz bed. It was found that the Ca/Sm₂O₃ material had higher activities for the oxidation of C₂H₆ and C₂H₄ (and also of CH₄) than had the Li/MgO material. These higher activities result in a lower optimal reaction temperature for the oxidative coupling of methane and are (at least partially) responsible for the lower selectivity to C₂ products observed with the Ca/Sm₂O₃ catalyst compared to that with the Li/MgO catalyst.

INTRODUCTION

The direct oxidative conversion of methane into products such as ethane and ethylene has recently attracted much attention [1-14] as an alternative route for the use of methane as a petrochemical feedstock. Two types of process, cyclic and co-feed, have been proposed in the literature for the oxidative coupling process. Each of these requires specific catalyst formulations. Catalysts which have proved to be successful for the cyclic variant of the process are supported metal oxides (e.g. Mn₂O₃ supported on SiO₂), often promoted with an alkali metal ion [2]. The co-feed version has attracted the attention of a great number of research groups and a variety of catalyst systems have been used [3-9]. In a recent publication [11], we have suggested that the stabilities of the desired C₂-hydrocarbon products (C₂H₆ and C₂H₄) play an important role in determining the all-over selectivities and yields of the reaction under the co-feed conditions. Jones et al. [2] and Labinger and Ott [10] have previously reached similar conclusions for the cyclic operation mode.

Some investigations concerning the stability of the C₂ products have been reported. For example, Ito et al. [4] have studied the rate of oxidation of

ethane relative to the that of methane over a Li/MgO catalyst at a temperature of 620°C. Otsuka et al. [5] have compared the rates of oxidation of both ethane and ethylene with that of methane in the presence of a Sm_2O_3 catalyst at 610°C. Both sets of authors came to the conclusion that CO and CO_2 were produced mainly from the methane, in parallel to the formation of the C_2 products, under these conditions. However, the normal operating temperatures used for methane coupling for both these catalyst types are in the range 650-800°C. (If a hot spot is present in the catalyst bed, the maximum bed temperatures may be even higher [15].) Hence, the situation may be very different at these temperatures, for example, with respect to the gas-phase reactions.

This is the first of a series of interrelated papers in which we attempt to answer the question: what is the mechanism of the reaction and to what extent are the total oxidation products (CO and CO_2) formed by oxidation of the desired C_2 hydrocarbons? We have therefore investigated the reactivity with oxygen of ethane and of ethylene relative to that of methane when those molecules are fed with the methane. As catalysts we have used two of the most promising materials from the series which we have studied to date: Li/MgO and Ca/ Sm_2O_3 . The Ca-doped Sm_2O_3 catalyst was used instead of unpromoted Sm_2O_3 , as the doped catalyst showed improved selectivity and yield as well as a good stability compared to the undoped material [17]. Additionally, the oxidation reactions of ethane and ethylene (in the absence of methane) were examined in a gradientless reactor in order to give a further comparison of the two catalysts.

EXPERIMENTAL

Reaction Systems

The experiments described here were carried out in two separate sets of apparatus. The experiments of Figures 2 and 3 (see Results and Discussion) were performed in System 1, in which the reactor consisted of a fused alumina tube (4 mm i.d.) heated in an electric oven (40 cm heated length) and filled with 750mg of a Li/MgO or Ca/ Sm_2O_3 catalyst. The reactor feed consisted of a mixture of methane (67 kPa), oxygen (7 kPa) and nitrogen (26 kPa) with a total feed rate of $3.3 \text{ cm}^3\text{s}^{-1}$ (STP); ethylene (see Fig. 2) or ethane (see Fig. 3) was also added to the reactor feed. The reactor effluent was fed directly to a gas chromatograph which gave quantitative analysis of O_2 , N_2 , CH_4 , CO, CO_2 , C_2H_2 , C_2H_4 and C_2H_6 and qualitative analysis of H_2 and H_2O ; oxygenates and higher hydrocarbons were analysed off-line (see Results and Discussion).

The remaining experiments were performed using a recirculation apparatus, System 2 (see Figure 1), with a recirculation ratio (ratio of the recycle flow to the net flow through the system) of 30; the system thus behaves effectively as an ideally-mixed reactor system with respect to the gas-phase concentrations [18]. The quartz reactor tube, R (6mm i.d.), is placed in the recycle loop through which the

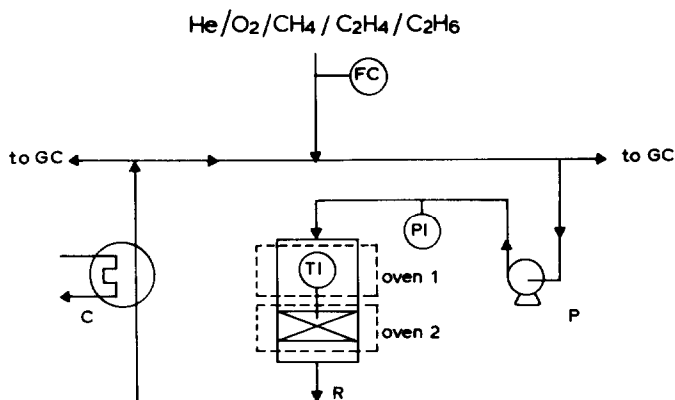


Figure 1. Schematic representation of the recycle reactor (System 2). FC, flow controllers; PI, pressure indicator; TI, temperature indicator; P, pump; C, cold trap

reactant gas mixture is recycled using a membrane pump, P. The pressure in the reactor is measured using a mercury manometer. Water vapour is condensed out of the reactor-effluent using a cold trap (C) maintained at 0°C, which is directly after the exit of the reactor. The flow rate of the fresh gas-feed mixture, either C₂H₄/O₂/He (6.8/8.5/84.7 kPa) or C₂H₆/O₂/He (6.5/8.5/85.0 kPa), is maintained at 0.13 cm³s⁻¹ (STP). A recirculation flow rate of 4 cm³s⁻¹ (STP) is used, resulting in a recirculation ratio of 30 (see above). The effluent from the system may be sampled for GC analysis at two positions in the recycle loop, before the reactor or after the cold trap; comparison of the gas composition at these two positions showed that the reactor is indeed practically gradientless, the oxygen concentrations (which show the largest variation) deviating less than 7% from the average value. The reactor tube passes through two ovens, each 10 cm long: the first is maintained at a temperature of 500°C to preheat the gas flow, and the second is at the desired reaction temperature. The catalyst bed (500 mg of catalyst, particle size 0.1-0.3 mm, bed length 14mm) is placed in the tube at the centre of the second oven and a thermocouple (in a quartz capillary) is located in the middle of the catalyst bed. For reasons of comparison, measurements without catalyst were also performed; in this case, in order to keep the residence time in the reactor the same, the catalyst bed was replaced by a bed of quartz particles of the same size. The effluent flow rates from the recirculation system are measured using a bubble meter. An axial temperature profile was recorded in the catalyst bed under operating conditions. The temperature profile was flat, the maximum deviation being 4°C from the average temperature. This is in marked contrast to the situation in a plug flow reactor in which we have frequently observed hot spots with temperature rises of up to 60 °C, depending on reaction

conditions. The temperatures given for the experiments of Figures 2 and 3 (System 1) are therefore the temperatures of the reactor wall rather than those of the catalyst bed.

Catalysts

The catalysts were prepared by wet impregnation [4, 13, 14, 17] of $\text{Mg}(\text{OH})_2$ with an aqueous solution of LiOH or of Sm_2O_3 with an aqueous dispersion of CaCO_3 . In the case of the Li/MgO catalyst, CO_2 was passed through the solution during evaporation of the excess solvent [13, 14]. After the evaporation step, the catalysts were dried at 140°C overnight and calcined at 850°C for 6 h. The resulting materials were crushed and sieved to give the desired particle size (0.1-0.3 mm). Analysis showed that the Li/MgO catalyst contained 2.8 wt% Li and 8.2 wt% CO_2 , while the $\text{Ca/Sm}_2\text{O}_3$ catalyst contained 4.5 wt% Ca and 2.2 wt% CO_2 .

RESULTS AND DISCUSSION

Addition of Ethylene and Ethane to a Gas Mixture Containing Methane and Oxygen

Figures 2 and 3 show the experiments which were performed in order to investigate the relative reactivity with oxygen of ethane or ethylene compared with that of methane. These experiments, using the Li/MgO catalyst at 800°C , were carried out in the single pass reactor (System 1) in which C_2H_4 or C_2H_6 was added to a reactor feed consisting of CH_4 , O_2 and N_2 ; similar experiments were also performed using the $\text{Ca/Sm}_2\text{O}_3$ catalyst (see below). The concentrations of the C_2 products (the sum of C_2H_6 and C_2H_4) and of the carbon oxides, CO_x (the sum of CO and CO_2), in the reactor effluent are given as a function of the concentration of ethylene and ethane in the reactor feed. The methane conversion, expressed as the difference in methane partial pressure between that of the feed and that of the effluent of the reactor (ΔCH_4), is also shown. ΔCH_4 is thus the absolute methane conversion. In experiments analogous to those of Figures 2 and 3, samples were taken from the reactor effluent and were analysed for components which could not be separated with the GC column used in the system; C_3 , C_4 and C_5 components were all identified but their concentrations were negligible.

The addition of ethylene to the reactor feed (Figure 2) resulted in an increase of the ethylene concentration in the reactor effluent and a simultaneous decrease in the ethane concentration; this resulted in an increase in the total C_2 concentration, as shown. A small increase of the concentration of the carbon oxides was also observed. The methane conversion was lowered by the addition of ethylene; total conversion of the oxygen was found for all these experiments. The decrease in ethane concentration and of the methane conversion with an increase in the amount of ethylene added to the feed shows that the added ethylene is being oxidised: the oxidation of this ethylene competes with the oxidative coupling of the methane for the available oxygen, lowering the methane consumption as well as the formation of ethane (a primary product of the coupling reaction). Under these

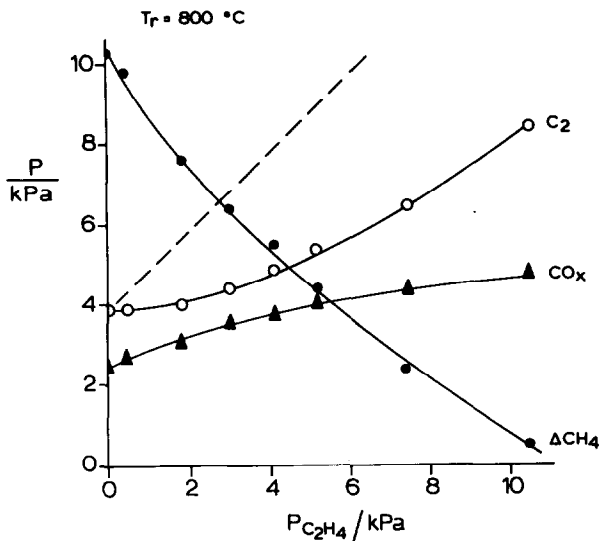


Figure 2. Product concentrations in the reactor effluent and the absolute methane conversion (ΔCH_4) as a function of the ethylene concentration in the reactor feed.

conditions, which are similar to those normally used for the oxidative coupling of methane, the reactivity of ethylene with oxygen is thus much higher than that of methane.

In the case of the addition of ethane (Figure 3), the concentrations of both the ethane and ethylene in the reactor effluent increased, resulting in an increase of the total concentrations of the C_2 hydrocarbons. The concentrations of CO and CO_2 increased only slightly. The conversion of oxygen was complete over the entire range of C_2H_6 concentrations, and the methane conversion was again decreased by the addition of the higher hydrocarbon. A relatively high concentration of ethylene was observed, this probably having been formed by the (oxidative) dehydrogenation of the added ethane. As this reaction consumes oxygen, this leaves less oxygen for total oxidation. It is thus to be expected that the levels of CO and CO_2 will be lower in the case of the addition of ethane than in that of the addition of ethylene, as is the case; compare Figures 2 and 3. As was the case for ethylene, the results of Figure 3 indicate that the reactivity of ethane with oxygen is also higher than that of methane.

That substantial oxidation of the C_2 products took place also follows from the total concentration of C_2 products in the effluent as a function of the concentration of ethane or ethylene in the feed. If the C_2 products were not oxidised and the coupling reaction of methane was not influenced by the addition of ethane or ethylene, the total C_2 concentration in the effluent would be the sum of the C_2 concentration produced from the methane and that of C_2H_4 or C_2H_6 added

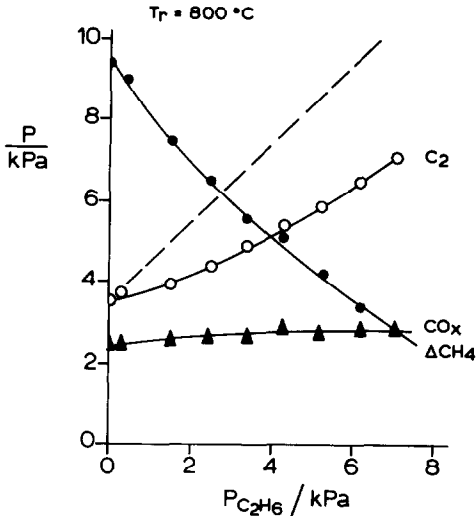


Figure 3. Product concentrations in the reactor effluent and the absolute methane conversion (ΔCH_4) as a function of the ethane concentration in the reactor feed. ethane with oxygen is also higher than that of methane.

to the feed. The plot of the variation of the C_2 concentration in the effluent as a function of added C_2 would thus be linear with a slope of one, with an intercept equal to the C_2 product concentration in the absence of added C_2 hydrocarbons (dotted lines in Figures 2 and 3). The fact that this is obviously not so in either case is thus added confirmation of the conclusion that total oxidation of the C_2 products must occur.

Experiments analogous to those shown in Figures 2 and 3 were performed with the Ca/Sm_2O_3 catalyst at different oven temperatures between 550 and 700°C. These experiments led to the same conclusions: the methane conversion is lowered by competition for the available oxygen between methane and the C_2 hydrocarbons.

Our conclusions are in contradiction to those of Ito et al. [4] and of Otsuka et al. [5], who studied the stability of the C_2 hydrocarbons, using Li/MgO and Sm_2O_3 catalysts respectively (reaction temperatures of 620°C and 610°C respectively) and concluded that the C_2 products were stable.

Oxidation of Ethane and Ethylene in the Recycle Reactor

As the oxidation of the C_2 products thus appears to make an important contribution to the product selectivity in the oxidative coupling of methane, it is of interest to examine whether or not the two catalyst formulations give different rates of total oxidation of the C_2 molecules. The rates of total oxidation of ethane and ethylene were therefore examined over both catalysts as well as in a quartz-filled reactor in the gradientless recycle system (see Figure 1).

The Oxidation of Ethylene. Figures 4 and 5 show the effect of reactor temperature on the oxidation of ethylene in the recycle reactor filled with quartz, Li/MgO or Ca/Sm₂O₃ catalyst particles; Figure 4 gives the conversions of oxygen and ethylene and Figure 5 shows the yields of CO and CO₂. In addition to the products shown in Figure 5, C₂H₆, C₂H₂ and CH₄ were also formed, the first two of these in low concentrations (< 2%); the production of methane was highest over Ca/Sm₂O₃, the yield being 15% at 800 °C.

(i) Quartz. The oxidation reaction of ethylene in the reactor filled with quartz particles (Figures 4 and 5) produces mainly CO, H₂O and H₂; CO₂ was a less important product. In a separate experiment (not shown here) in which the quartz particles were omitted, CO was also the main carbon oxide product; the conversion was now higher, presumably due to the longer residence time resulting from the larger gas volume of the reactor. We thus conclude that the quartz is largely inert and that the reactions taking place in the reactor packed with quartz particles are predominantly gas-phase reactions. The rates of the gas-phase oxidation reactions of ethylene in the reactor filled with quartz particles are low at lower temperatures (630-720°C) and increase sharply at higher temperatures; see Figure 4. These gas-phase reactions will also take place to some degree if the reactor is filled with catalyst particles, especially at the higher reaction temperatures.

The stability of ethylene was also studied in the absence of oxygen in an empty reactor (without quartz). Approximately 15% of the ethylene was lost at 800°C with the formation of C₂H₂, CH₄ and a carbonaceous deposit.

(ii) Li/MgO. The Li/MgO catalyst produces mainly CO₂; (Fig. 5) the production of hydrogen was much lower than that in the reactor filled with quartz particles. The results of Figure 4 show that there is a higher total rate of oxygen and ethylene consumption over the Li/MgO catalyst than in the case of gas-phase reaction at almost all temperatures (see below); the activity is relatively low at the lower temperatures of the range studied but increases relatively sharply with temperature. Above about 790°C, the Li/MgO catalyst gave a lower rate of ethylene oxidation than found in the experiment with quartz (see Figure 4). This was probably caused by the different product selectivities in the two cases, CO₂ being the main product over the Li/MgO catalyst, and CO being the main product in the gas-phase reactions; as the oxygen was almost depleted at 790°C in the case of the Li/MgO catalyst, less oxygen was available for the oxidation of ethylene.

(iii) Ca/Sm₂O₃. The Ca/Sm₂O₃ catalyst was found to be a relatively very active oxidation catalyst: the oxygen conversion is almost 100% over the entire temperature range of 630-810°C (Figure 4) and hence the C₂H₄ conversion remains above that of the gas-phase reaction over the whole range. Compared with the Li/MgO catalyst, the Ca/Sm₂O₃ catalyst produces substantially more CO.

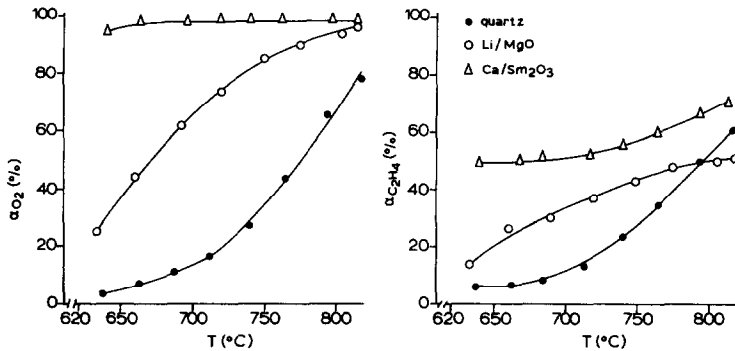


Figure 4. Oxygen and ethylene conversion as a function of the reaction temperature in the reactor of System 2 filled with quartz, Li/MgO or Ca/Sm₂O₃ particles.

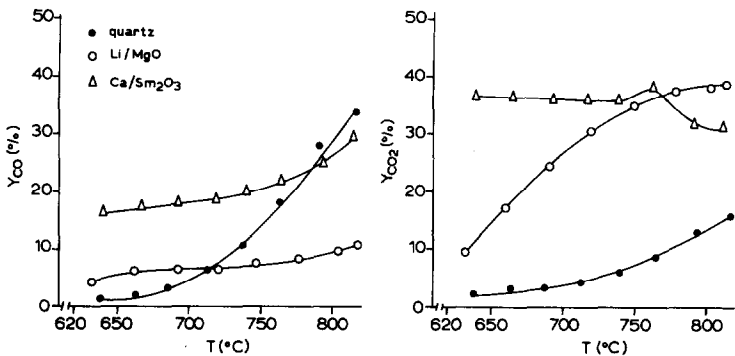


Figure 5. Yield of CO and CO₂ as a function of the reaction temperature in the reactor of System 2 filled with quartz, Li/MgO or Ca/Sm₂O₃ particles.

The Oxidation of Ethane. Figures 6 and 7 show, again as a function of temperature, the results for the oxidation of ethane in the reactor filled with quartz, Li/MgO, or Ca/Sm₂O₃ particles. Figure 6 shows the conversions of oxygen and ethane; as ethylene was formed as an additional product in these cases, its yields are also given. Figure 7 shows the yields of CO and CO₂. Besides the products shown in these figures, C₂H₂, CH₄ and H₂ were also produced, the concentrations of C₂H₂ and CH₄ being approximately the same as in the oxidation of ethylene; however, the hydrogen concentration was higher for the oxidation of ethane than for that of ethylene if the reactor was packed with quartz particles, presumably due to non-oxidative dehydrogenation of the ethane. With both of the catalyst systems, the rate of hydrogen production in the oxidation of ethane was approximately the same as that in the case of ethylene. The hydrogen production from ethane in the presence of both of the catalysts was lower than in the case of quartz particles for temperatures above 700 °C.

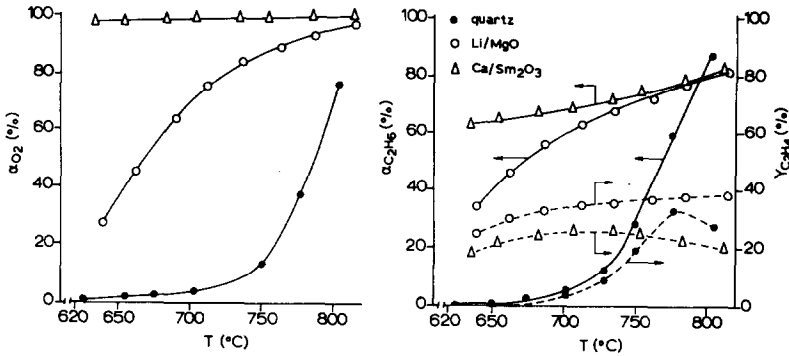


Figure 6. Oxygen and ethane conversion and ethylene yield as a function of the reaction temperature in the reactor of System 2 filled with quartz, Li/MgO or Ca/Sm₂O₃ particles.

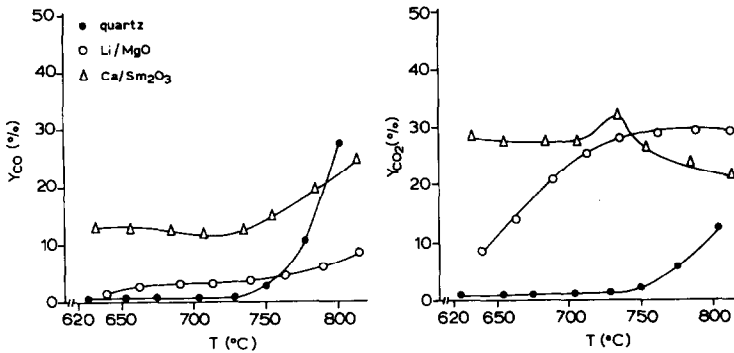


Figure 7. Yield of CO and CO₂ as a function of the reaction temperature in the reactor of System 2 filled with quartz, Li/MgO or Ca/Sm₂O₃ particles.

(i) Quartz. The rate of the gas-phase oxidation reaction of ethane is low at relatively low temperatures (620-750°C) but increases sharply with temperature in the region 750-810°C (Figure 6), presumably due to a high activation energy. The main carbon containing product of the gas-phase oxidation of ethane at lower temperatures is ethylene, but the main product at higher temperatures is CO. The yield of ethylene rises with the conversion of ethane as a function of temperature until about 770°C, as shown in Figure 6; above this temperature, the ethylene yield starts to decline, due to the further oxidation of the ethylene produced, and the oxygen conversion increases correspondingly steeply. In an experiment (not shown here) involving pyrolysis of ethane in the absence of oxygen in the reactor filled with quartz particles (with the same ethane concentration in the feed as in the oxidation experiments), a remarkably high ethylene yield was found: 25% at 730°C and 52% at 810°C. The ethylene production from ethane started at the same temperature as in the experiment with oxygen present and it may thus be that the

non-oxidative dehydrogenation of ethane to ethylene is rate determining for the case of oxidation without a catalyst.

(ii) Li/MgO. The presence of the Li/MgO catalyst had the same effect on the rate of oxidation of ethane (Figure 6) as was observed for ethylene (Figure 4). The conversion of oxygen was approximately the same in both cases; however the conversion of ethane was higher than that of ethylene at all temperatures. This difference is related to the different stoichiometries of the reactions taking place, ethylene also being a product during the conversion of ethane. As the (oxidative) dehydrogenation of ethane to give ethylene consumes little oxygen, this results in a higher conversion of ethane relative to that of ethylene at a given oxygen conversion. As with ethylene, the main carbon oxide produced from ethane by the Li/MgO catalyst is CO_2 .

(iii) Ca/Sm₂O₃. The Ca/Sm₂O₃ catalyst was again the most active oxidation catalyst, resulting in a complete oxygen conversion over almost the whole temperature range studied. The yield of ethylene was lower than with the Li/MgO catalyst despite the fact that the Ca/Sm₂O₃ catalyst showed a higher ethane conversion. This is probably caused by a higher rate of oxidation of the C_2H_4 formed over the Ca/Sm₂O₃ catalyst than over the Li/MgO catalyst. The high total oxidation rate found for ethylene over the Ca/Sm₂O₃ catalyst (see Figures 4 and 5) supports this explanation.

It is clear from the above results that the oxidation reactions of ethane and ethylene occur readily over both catalysts. Further, the Ca/Sm₂O₃ catalyst shows an oxygen conversion of practically 100% over the whole temperature range used for these experiments. The Li/MgO catalyst is less active for total oxidation and the ethylene yield in the dehydrogenation of ethane is higher when compared to the Ca/Sm₂O₃ catalyst, probably as a result of its lower rate of total oxidation of ethylene.

At the lower temperatures of the range studied, the rate of oxidation of ethane and ethylene in the gas-phase appears to be relatively low, and the presence of a catalyst increases the oxidation rates; however at temperatures around 800°C, the rates of the gas-phase oxidation reactions increase sharply until they are comparable with those of the catalytic reactions.

Consequences for the Reaction Network.

Before detailed conclusions can be drawn about the relative contributions of the total oxidation reactions of the C_2 hydrocarbons to the formation of the total oxidation products (CO and CO_2) during the oxidative coupling of methane, the rates of oxidation of the C_2 hydrocarbons must be compared with the rates of formation of these compounds during coupling and with the rates of the oxidation of methane directly to the carbon oxides. The experiments shown in Figures 4-7 can only be interpreted as showing the relative oxidation activities of the catalysts: under oxidative coupling conditions, the situation will be different, methane

being present in high concentrations. It has been argued that the presence of excess methane has a significant inhibiting effect on the rates of gas-phase oxidation reactions of C_2 molecules [19]; results of experiments confirming this suggestion will be discussed in detail in a following publication [16]. However, the results of the experiments shown in Figures 1 and 2, (in which the methane was also present in high concentrations) indicated that extensive oxidation of ethane and ethylene also takes place in the presence of excess methane; this implies that the oxidation reactions of the C_2 products have a significant effect on the selectivities for the oxidative coupling of methane. The negative effect on the C_2 selectivities of back-mixing of both reactants and products pointed to the same conclusion [11]. The present results allow us to draw a parallel between the high activities for total oxidation of ethane and ethylene observed with the Ca/Sm_2O_3 catalyst and the lower selectivity of this catalyst for the oxidative coupling of methane compared with that of the Li/MgO catalyst [17]. The activity of the Ca/Sm_2O_3 catalyst for methane activation is higher than that of Li/MgO and so the Ca/Sm_2O_3 catalyst is active at lower reactor temperatures: in System 1, using the process conditions given in the experimental section, the Ca/Sm_2O_3 catalyst reaches a conversion of 14% at a reactor temperature of 675°C, whereas the Li/MgO sample needs a reactor temperature of 800°C to attain the same conversion. As a result of this higher activity, however, the rate of oxidation of the C_2 compounds over the Ca/Sm_2O_3 catalyst is also higher than with the Li/MgO sample, resulting in a lower selectivity (70% in the case of the Ca/Sm_2O_3 catalyst, under the conditions given above, as opposed to 83% using the Li/MgO material).

CONCLUSIONS

1. The total oxidation reactions of ethane and ethylene make important contributions to the all-over reaction network for the oxidative coupling of methane over a Li/MgO or Ca/Sm_2O_3 catalyst.
2. The higher activity of the Ca/Sm_2O_3 catalyst as compared to the Li/MgO catalyst for the oxidation (to CO and CO_2) of ethane and ethylene is at least partially responsible for the lower selectivity of the former sample.

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