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Citation for published version (APA):

Geerts, J. W. M. H., Kasteren, van, J. M. N., & Wiele, van der, K. (1989). The investigation of individual reaction steps in the oxidative coupling of methane over lithium doped magnesium oxide. *Catalysis Today*, 4(3-4), 453-461. <https://doi.org/10.1016/0920-5861%2889%2985041-2>

DOI:

[10.1016/0920-5861%2889%2985041-2](https://doi.org/10.1016/0920-5861%2889%2985041-2)

Document status and date:

Published: 01/01/1989

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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THE INVESTIGATION OF INDIVIDUAL REACTION STEPS IN THE OXIDATIVE COUPLING OF METHANE OVER LITHIUM DOPED MAGNESIUM OXIDE

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ABSTRACT

To elucidate the importance of various reaction steps in the oxidative conversion of methane, experiments were carried out with three reaction products: ethane, ethylene and carbon monoxide. These products were studied separately in oxidation experiments with and without a catalyst. Moreover, the effect of admixing them to a methane/oxygen feed was investigated. All experiments were carried out in a micro flow tubular quartz reactor which was either empty or filled with catalyst at a temperature of 800 °C. The ethane and ethylene experiments showed that the conversion of ethane to ethylene is much more rapid than ethane combustion, irrespective of the presence of a catalyst. The main combustion path goes via ethylene. Ethane is converted much more rapidly than methane and this imposes serious constraints on the maximum attainable yields. The principal combustion product in the absence of a catalyst is CO but with a catalyst, CO₂ dominates, in agreement with rapid catalytic oxidation observed with CO/O₂ feeds.

The conclusions are summarized in a simplified overall reaction scheme.

INTRODUCTION

Since about 1980, the catalytic direct methane conversion has received renewed attention due to the development of some quite active and selective catalysts [1,2,3,4]. The most successful catalyst until now is "lithium doped magnesia", introduced by Lunsford in 1985 [5]. Since then much research has been focused on this catalyst system and it is clear that C₂⁺ yields up to 19% are possible at temperatures of 800°C [5]. At the high reaction temperatures needed to operate the catalyst, non-catalytic gas phase reactions occur and play an important role in the reaction mechanism. In this study, methane oxidation has been investigated over a lithium/magnesium oxide catalyst by single reaction steps analysis.

EXPERIMENTAL

All experiments were carried out in the reactor set-up shown in Figure 1. The heart of this apparatus is a quartz micro fixed-bed reactor (Figure 2) operated at 1 atm.

Feed section Reactor section Analytic section
Figure 1: Flow diagram of the laboratory set-up.

After heating up of the catalyst to the desired reaction temperature, typically 800 °C, under a flow of helium a reaction gas was introduced. Typical flow rates were 100 cm³/min consisting of methane (Hoekloos 99.6%) 50 cm³/min, oxygen (Hoekloos 99.9%) 10 cm³/min and helium (Hoekloos >99.995%) 40 cm³/min. In the admixing experiments, ethylene (Hoekloos 99.8%) or ethane (Hoekloos 99.3%) was added at the cost of helium so that the total flow rate did not change. The experiments were carried out after the catalyst (1 g) had stabilized (48 h). The carbon monoxide (Hoekloos) used was 99.5% pure.

The product gases were analyzed by gas chromatography. The column packings were Porapak R (3m) for the separation of CH₄, CO₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈ and H₂O and a 5-A molecular sieve (3m) for the separation of H₂, O₂, CH₄ and CO. The porapak was operated at 70°C and the molecular sieve at 110°C. Both columns were connected to a Thermal Conductivity Detector (TCD) and helium was the carrier gas. With this method, a carbon balance of 98% was achieved.

The catalyst was made by slurring Li_2CO_3 and MgO in water and evaporating the water until dryness. The quantities of Li_2CO_3 and MgO were calculated to produce a 7 wt% $\text{Li}/(\text{Li}+\text{MgO})$ catalyst. Drying of the catalyst took place at 120°C for 24 hours. After this, the catalyst was calcined at 900°C for 4 hours and then crushed and sieved to the desired particle size (preferably 0.4-0.6 mm).

Figure 2: The tubular quartz reactor.

RESULTS & DISCUSSION.

Experiments were carried out with a cofeed of ethane or ethylene and oxygen. Conditions were chosen similar to those used in methane oxidative coupling experiments.

First, experiments were carried out in an empty reactor. The results are shown in Figure 3. It appears that ethane is oxidised much easier than methane, which starts to be converted at a much higher temperature (A figure is not shown; the temperature difference is more than 150°C). The main product is ethylene. Ethylene is oxidised even faster than is ethane, the main product being CO . The difference in oxidation rate between ethane and methane correlates with the difference in C-H bond strength in these molecules (CH_4 : 104 ± 1 kJ/mole, C_2H_6 98 ± 1 kJ/mole), and the fact that hydrogen abstraction undoubtedly is the rate determining step. The high reactivity of ethylene must be due to the fact that oxygen or oxygen-containing radicals attack the double bond. The fact that the conversion level of ethylene is lower than that of ethane is not reflecting kinetics. The only reason is that oxygen consumption is complete in both cases and that the oxidation of ethylene consumes much more oxygen per hydrocarbon molecule than does that of methane.

Figure 3: Ethane oxidation Ethylene oxidation
 Selectivities and conversions as a function of the reaction
 temperature for gas phase oxidation experiments. $C_2/O_2=2.2$,
 $He/C_2=8.5$.

Similar experiments were next carried out in a reactor filled with the lithium/magnesium oxide catalyst.

The results are surprisingly similar to those just described, except for a remarkable shift in the selectivities with respect to the carbon oxides, as shown in Figure 4. The oxidation of CO to CO₂ is apparently strongly accelerated by the catalyst. Additional evidence stems from a similar shift that was observed during the deactivation of the catalyst in the methane oxidation experiments (Figure 5).

Direct proof of the activity of the catalyst for CO oxidation is produced by separate CO oxidation experiments, as shown in Figure 6. Initially, very high rates are achieved with a catalyst. Significant deactivation occurs, which may be explained by poisoning of the catalyst by CO₂, as proven by Korf et al. [7].

Ethane oxidation
Difference: gas phase - catalyst

Ethylene oxidation
Difference: gas phase - catalyst

Figure 4: Ethane oxidation Ethylene oxidation
Differences in conversions and selectivities between gas phase and catalytic C₂ oxidation experiments. C₂/O₂=2.2, He/C₂=8.5, W/F= 0.6 g.s/Nml

Figure 5: Catalyst deactivation
Time on stream for a Li/MgO catalyst. T=800°C, W/F=0.6 g.s/Nml, CH₄/O₂=10.

Figure 6: CO oxidation
Gas phase and catalytic oxidation of CO. T=800°C, W/F=0.3 g.s/Nml, CO/O₂=4, CO/He=0.06

However, even after catalyst deactivation, the conversion level of CO is an order of magnitude larger than in the absence of the catalyst.

Although the oxidation of ethane and ethylene separately fed to the reactor gives valuable information, cofeeding with methane is even more interesting. Ethane is present in natural gas, and moreover, recycling of the ethane is of interest to improve the ethylene yield. Cofeeding of ethylene is particularly useful to obtain more reliable data on its stability (its relative reactivity with respect to methane) under actual reaction conditions.

The results of ethane and ethylene cofeeding (Figure 7) show remarkable similarities. All the corresponding curves in these figures have practically the same shape. It seems to make no difference whether ethane or ethylene is fed to the methane/oxygen flow. Apparently, ethane is rapidly converted into ethylene, maybe even before methane oxidation starts.

The top diagrams in Figure 7 show the actual concentrations

Figure 7: Addition of ethane Addition of ethylene
Mol fractions at the outlet of the reactor of admixing of C₂ to a methane/oxygen/helium mixture, catalysed by Li/MgO. T=800°C, CH₄/O₂=10, W/F=0.6 g.s/Nml.

of methane and hydrogen, corrected for the small changes in the total volume that occurs. The feed gas contains 45 mol% of methane; the shaded area therefore represents the methane conversion. It is clear that the addition of C_2 's to the feed stream decreases the methane conversion, because part of the oxygen available is consumed by the C_2 's added. The two extra hydrogen atoms of ethane, in comparison to ethylene, cause somewhat higher hydrogen and water concentrations at the outlet of the reactor than in the case of ethylene addition. Furthermore, it is shown that the more C_2 is added, the more carbon monoxide is produced, which is in agreement with the ethylene experiments; see Figure 3. This CO is oxidised further to CO_2 , the production of which also increases. However, at high added mol fractions, the oxygen is used by C_2 's before CO can be oxidised, and this results in a diminished CO_2 production.

The C_3 concentrations are shown a hundred-fold magnified in Figure 7. No C_4 -products could be detected. The C_3 production is enhanced by C_2 cofeeding, but the amounts formed remain relatively small. Methane oxidation thus appears to be a rather selective process for the production of ethylene, particularly if ethane is recycled. One should realize however, that the net C_2 production rapidly decreases when ethane is added. It is already zero at an added mol fraction ethane of 2 %.

CONCLUSIONS

It is believed that the oxidative methane coupling mainly occurs via radicals and that an appreciable part of the reaction sequence takes place in the homogeneous gas phase. A simplified scheme is shown in Figure 8. The bold arrows indicate the main reaction path, as emerges from our results.

The catalyst plays an essential role in at least two reaction steps: besides the initiation reaction, the oxidation of CO to CO_2 is also catalysed, as is established in this work. As it is known that high initial ethane selectivities can be achieved [4,5], $CH_3\cdot$ radicals apparently first combine to ethane. This ethane is then very rapidly converted into ethylene, which is further oxidised into carbon monoxide either directly or via formaldehyde. The C_3 products play a minor role in this mechanism due to their low formation rates. Calculations with a computer simulation program, not presented here, have confirmed this.

Figure 8:
Proposed reaction scheme.

Figure 9:
Selectivity as a function of
the CH_4 conversion, for
parallel and consecutive side
reactions

In conclusion, it can be said that the conversion of methane to C_2 is relatively slow in comparison to the oxidation of C_2 into CO . This puts serious constraints on the maximum attainable yield. A graphical representation of the attainable yield as a function of conversion is given in Figure 9, this is calculated according to the simplest parallel-consecutive reaction scheme, and assumes that all reactions are first order with respect to oxygen [9]. The data points in Figure 9 show that the catalyst studied here corresponds to $k_2/k_1 = 0.25$ (initial selectivity = 80%) and $k_3/k_1 = 3$.

Both excellent initial selectivities and low relative combustion rates of ethylene are required to obtain high selectivities at a reasonable conversion level. The relative combustion rate of ethylene, in particular, deserves more attention in catalyst evaluation studies.

ACKNOWLEDGEMENT

The financial support for this research, which was provided by the Netherlands Organization for Scientific Research (NWO), and by the European Communities under contract no. EN3C-0038-NL, is gratefully acknowledged.

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