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# Methane oxidative coupling on the $Au/La_2O_3/CaO$ catalyst in the presence of hydrogen peroxide

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Methane oxidative coupling in the presence of the catalyst 1% Au/5% $La_2O_3/CaO$ and gas-phase initiator hydrogen peroxide at the temperature 700–800°C under normal pressure has been studied. It has been shown that hydrogen peroxide remarkably increases the yield of $C_{2+}$ products without the loss of selectivity. The maximal yield of $C_{2+}$ products under the conditions studied was 27% with the formation of a noticeable quantity of benzene. It has been proposed, that the observed effect is due to hydroxyl radical formation from hydrogen peroxide, which could be essential under definite conditions also in a conventional catalytic methane oxidative coupling.

**Keywords:** methane oxidative coupling; hydrogen peroxide; gas-phase initiation

## 1. Introduction

Oxidative coupling of methane using air or pure oxygen as the oxidant, has been intensively studied in the last decade and still provides the best practical solution for direct methane conversion into more valuable products, although the yield is still not high enough for commercialisation [1]. Research efforts have been directed mostly towards a search for new catalysts and the optimization of reaction conditions. Attempts to use other oxidants such as nitrous oxide instead of oxygen have not led to an improvement in the yield of $C_{2+}$ products [2].

Recently, it has been shown that hydrogen peroxide can serve as an oxidant as well as an initiator for homogeneous non-catalytic methane oxidative coupling without a catalyst at a temperature as low as 400°C [3]. (Methane oxidation by hydrogen peroxide has also been reported in refs. [4,5].) On the other hand, hydrogen peroxide can be formed in situ under the conditions of catalytic methane oxidative coupling. Indeed, hydrogen peroxide formation in the process of methane

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oxidative coupling could explain the effect of reaction mixture quenching observed to take place in the region after the catalytic bed [6].

Taking into account the two above mentioned possibilities of acceleration of the methane oxidative coupling, using together a catalyst and a gas phase initiator in the reaction appears attractive.

In this study the methane oxidative coupling over a gold–lanthanum–calcium oxide catalyst in the presence of hydrogen peroxide has thus been investigated.

## 2. Experimental

Experiments were carried out in a continuous-flow installation using a fixed-bed reactor with a catalyst loading of 0.7 g. Analysis was performed using two on-line GCs. One comprised of a FID GC and a 2 m Porapak Q column for analysis of hydrocarbons below $C_6$. The second GC comprised of a TCD and two columns: a 2 m Carbosieve II column for CO and $CO_2$ analysis and a 1 m molecular sieve 13X column for oxygen and nitrogen analysis. Nitrogen was used as a marker to determine changes in the reaction mixture volume during the reaction. Heavy hydrocarbons ($C_{6+}$) were collected in a trap after the reactor and were analyzed by an off-line GC with a 30 m DB5 capillary column.

The 1% Au/5% $La_2O_3/CaO$ catalyst was prepared by impregnation of lanthanum–calcium oxide with a solution of $AuCl_3$ in absolute ethyl alcohol. The lanthanum–calcium oxide (5 wt% $La_2O_3/CaO$) was prepared by wet mixing of appropriate quantities of lanthanum oxide and calcium oxide (CP grade, BDH) followed by drying overnight at 120°C and calcination at 800°C for 6 h.

## 3. Results and discussion

The reaction was studied in the temperature range 700–800°C under normal pressure with the reaction mixture: methane 100, oxygen 45 and nitrogen 10 ml/min. An aqueous solution of hydrogen peroxide with concentrations varying from 2.6 to 21 wt% or pure water was added to the reaction mixture via an evaporator at a rate of 0.03 ml/min.

The results of the experiments with water, hydrogen peroxide as well as without any liquid addition to the feed are presented in table 1.

It can be seen from table 1, that without any liquid addition the maximal yield of $C_{2+}$ products under the reaction conditions was about 12% at a conversion of 32%. The addition of pure water increased the maximal yield to 17%. This increase in yield was due to a rise in the total selectivity of $C_{2+}$ products as well as an increase in the methane conversion. The formation of a small quantity of benzene was observed. (The rise in conversion could be related to dilution of the reaction mixture by water vapour [7].)

Table 1
Influence of hydrogen peroxide on the methane oxidative coupling reaction over a 1% Au/5% $La_2O_3$/CaO catalyst. (gas (in ml/min): $CH_4$ – 100, $O_2$ – 45; liquid – 0.03 ml/min; catalyst – 0.7 g)

| *T* (°C) | Liquid | Conv. of $CH_4$ (%) | Selectivity (%) | | | Yield of $C_{2+}$ (%) | $C_2^{=}/C_2^{-}$ |
|---|---|---|---|---|---|---|---|
| | | | $C_2$ | $C_{3,4}$ | $C_6H_6$ | | |
| 700 | none | 31.6 | 33.8 | 1.1 | – | 11.0 | 1.30 |
| 800 | | 32.3 | 35.8 | 1.2 | – | 11.9 | 2.18 |
| 700 | $H_2O$ | 32.5 | 44.9 | 1.4 | 5.5 | 16.8 | 1.21 |
| 800 | | 32.9 | 44.6 | 1.7 | 6.6 | 17.4 | 1.74 |
| 700 | $H_2O_2$ | 35.4 | 45.2 | 1.8 | 9.9 | 20.1 | 1.25 |
| 800 | (2.6%) | 35.9 | 45.1 | 2.1 | 12.0 | 21.3 | 1.90 |
| 700 | $H_2O_2$ | 35.8 | 48.2 | 1.9 | 10.3 | 21.6 | 1.35 |
| 800 | (7.6%) | 36.0 | 47.7 | 2.4 | 12.9 | 22.7 | 2.00 |
| 700 | $H_2O_2$ | 35.9 | 48.4 | 2.3 | 16.2 | 24.0 | 1.50 |
| 800 | (21%) | 38.1 | 48.2 | 3.4 | 19.2 | 27.1 | 2.11 |

The addition of hydrogen peroxide to the reaction mixture caused an increase in the methane conversion as well as the selectivity of the $C_{2+}$ products, which resulted in yield enhancement. The higher the concentration of added hydrogen peroxide, the higher the methane conversion and the higher the yield of $C_{2+}$ of products obtained (table 1).

A peculiarity of the reaction, under the reaction conditions, was the formation of a noticeable quantity of benzene. This could be related to an acceleration of the process of olefin aromatization by hydrogen peroxide as well as by the metal component (gold) of the catalyst. The maximal yield of $C_{2+}$ products obtained was 27% with a corresponding 7% yield of benzene.

The increase of hydrogen peroxide concentration also resulted in an increase in the ethylene/ethane ratio in the reaction products when compared with pure water. (The higher ethylene/ethane ratio in the experiment without any liquid addition could be due to the lack of benzene formation under these conditions, as ethylene is likely to be the precursor of the aromatic product [8].)

The influence of hydrogen peroxide could be related to formation of hydroxyl radicals in the reaction,

$$H_2O_2 + M \rightarrow 2OH$$

The hydroxyl radical could interact directly with methane to form a methyl radical,

$$CH_4 + OH \rightarrow CH_3 + H_2O\,,$$

as well as provide an initiation route to a chain-branching process,

$$OH + H_2 \rightarrow H_2O + H$$

$$H + O_2 \rightarrow OH + O$$

$$O + H_2 \rightarrow OH + H\,,$$

which could be important at low oxygen conversions. According to ref. [9], hydroxyl radicals contribute more to the methyl radical formation under conditions of homogeneous methane oxidative coupling.

The above reaction pathway for methyl radical formation could also be important for the conventional catalytic methane oxidative coupling reaction, where the formation of hydrogen peroxide could occur in situ by the reaction

$$CH_4 + HO_2 \rightarrow CH_3 + H_2O_2$$

(The $HO_2$ radical could be formed by several reactions, but according to ref. [9], mainly via oxidation of the formyl radical.)

The in situ hydrogen peroxide formation could explain the effect of reaction mixture quenching on methane conversion and the $C_2$ product formation, observed in ref. [6]. Due to the high activation energy the rate of the hydrogen peroxide dissociation reaction slows down sharply with a decrease in the temperature resulting in a blockage of the additional channel to methyl radical formation.

## 4. Conclusion

The present study shows that methane conversion and the yield of $C_{2+}$ products can be remarkably enhanced by hydrogen peroxide, which can serve as a gas-phase initiator for methyl radical formation, presumably by generation of OH radicals. This channel to methyl radical formation can also be important for the conventional catalytic methane oxidative coupling reaction, where hydrogen peroxide could be formed in situ. This would lead to a degenerate chain-branching reaction in the postcatalytic zone resulting in an additional amount of $C_2$ product being formed [6].

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