# Low temperature catalytic partial oxidation of methane for gas-to-liquids applications

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## Abstract

The catalytic partial oxidation (CPO) of methane in the presence of steam (low temperature catalytic partial oxidation, LTCPO) over noble metal catalysts was investigated. The "dry" CPO over ruthenium and rhodium catalysts was studied by thermogravimetric analyses coupled with IR spectroscopy. For CPO conditions, high CO selectivities at comparably low temperatures were observed for a rhodium/γ-alumina catalyst (5% rhodium) and a 1% ruthenium/TiO$_2$ catalyst giving evidence that a direct reaction mechanism is involved at low temperatures. It was found that under CPO conditions at low temperatures (<450 °C) the catalysts are in an oxidised state, which is probably responsible for the formation of carbon dioxide. At higher temperatures, the catalysts are in a reduced state. The CO selectivity increases with the reduction of the catalyst. Our results indicate that a direct CO formation mechanism is also possible for ruthenium/alumina catalysts.

The platinum catalysts studied in the LTCPO of methane were less active than rhodium and ruthenium catalysts and revealed a lower hydrogen yield. It was found that the steam reforming activity of the ruthenium/alumina catalyst was reduced inhibited by ceria. The long term stability (80 h) of a ruthenium catalyst for LTCPO of methane was demonstrated.
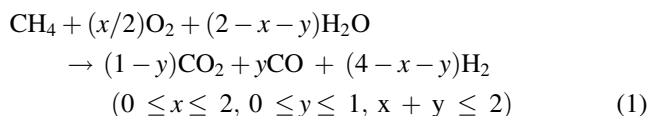© 2005 Elsevier B.V. All rights reserved.

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## 1. Introduction

The use of methane as an alternative feedstock for the generation of clean transportation fuels by gas-to-liquids (GTL) technology has gained considerable interest during the last decade [1,2]. GTL technology is coupling reforming reactions of methane to synthesis gas (CO and H$_2$) and Fischer–Tropsch synthesis (FTS) to liquid transportation fuels (i.e. synthetic diesel, synfuel). These transportation fuels are free of sulphur and aromatic hydrocarbons and reduce exhaust emissions. Ideally, the syngas produced has the same stoichiometry as the final product. For processes that convert CO$_2$ into liquid hydrocarbons this is expressed by the module $M = (H_2–CO_2)/(CO + CO_2)$ [3]. For the production of Fischer–Tropsch liquids $M$ should have a value of 2.1.

In general, the partial oxidation and reforming reactions can be summarized according to Eq. (1):

$$CH_4 + (x/2)O_2 + (2 - x - y)H_2O$$
$$\rightarrow (1 - y)CO_2 + yCO + (4 - x - y)H_2$$
$$(0 \leq x \leq 2,\ 0 \leq y \leq 1,\ x + y \leq 2) \quad (1)$$

The production of CO and CO$_2$ is controlled by the thermodynamic equilibrium. For high temperatures, $y$ values are close to 1 and CO is mainly produced. At low temperatures, $y$ is close to 0 and CO$_2$ is mainly formed.

The most cost-intensive part of a GTL is the generation of synthesis gas [4]. Synthesis gas is currently produced by steam reforming (SR) of natural gas or naphtha. However, steam reforming is a highly endothermic reaction and produces a synthesis gas with an H$_2$/CO ratio of 3 assuming complete conversion of methane (Eq. (2)):

$$CH_4 + H_2O \rightarrow CO + 3H_2, \quad \Delta H_R^\circ = 206\,kJ/mol \quad (2)$$

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For Fischer–Tropsch synthesis an $H_2/CO$ ratio about 2.1 is desired. Thus, for FTS the excess hydrogen would have to be separated.

A proposed alternative route of syngas production is autothermal reforming (ATR). This process is a combination of homogeneous partial oxidation ("partial combustion") and catalytic steam reforming. The process operates at high temperatures (around 2000 °C in the combustion zone and 1200 °C in the catalytic zone) [5]. Thus, materials with a high thermal stability are required and increase capital and operating costs for a GTL plant.

Efforts have been made to decrease the process temperatures by direct catalytic partial oxidation (CPO, Eq. (3)) [6]. CPO is a mildly exothermic process. The $H_2/CO$ ratio is 2 which is close to the ideal one for Fischer–Tropsch synthesis:

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2, \quad \Delta H_R^\circ = -36\,kJ/mol \quad (3)$$

Ni-based catalysts were investigated for this process [7–9]. Later, different noble metal catalysts (Pt, Pd, Rh, Ru) were successfully investigated [10–15]. CPO operates at temperatures around 800 °C. For GTL applications, oxygen instead of air has to be used as oxidant in order to avoid the dilution of the FT synthesis feed by nitrogen. The use of oxygen instead of air creates safety problems and increases costs due to the cryogenic air separation unit.

An alternative FT synthesis feed is provided by a low temperature "wet" catalytic partial oxidation (LTCPO). This process is a combination of endothermic steam reforming and exothermic CPO. As can be derived from Eq. (1), with $x = 1$ and $y = 0$, a $CO_2$ rich syngas can be formed (Eq. (4)):

$$CH_4 + 0.5O_2 + H_2O \rightarrow CO_2 + 3H_2, \quad \Delta H_R^\circ = -77\,kJ/mol \quad (4)$$
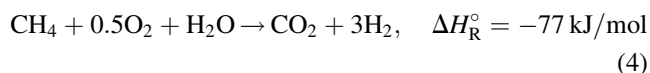
Thermodynamic equilibrium calculations according to Eq. (1) for $x = 0$ (steam reforming), $x = 1$ (LTCPO), $x = 2$ (CPO with an oxygen-to-carbon ratio of 2) and $y = 0$ as input reveal the influence of $x$ on methane conversion, $CO_2$ yields, $M$ factor and reaction enthalpy (Fig. 1).

The highest methane conversions in the low temperature regime (<700 °C) are observed at oxygen rich conditions. However, the calculated $M$ factors are far too small for GTL applications. The reaction is strongly exothermic. In contrast, steam reforming is strongly endothermic and produces an $M$ factor of 3. The methane conversions are comparably lower. The LTCPO ($x = 1$) reveals reasonable methane conversions and suitable $M$ factors close to 2. Around 650 °C, the reaction is mildly exothermic. Thus, the addition of water decreases the formation of hot spots. Applying steam-to-carbon ratios (S/C) higher than the calculated ones (calculated: S/C = 1 for $x = 1$ and $y = 0$) increases the methane conversion because the reaction rate of steam reforming at low temperatures depends strongly on the S/C ratio [16].

Due to the lower temperatures, the LTCPO process produces a $CO_2$ rich synthesis gas. Thus, an advanced Fischer–Tropsch process is required which also converts $CO_2$ into Fischer–Tropsch liquids. Iron catalysts exhibit promising properties for the hydrogenation of $CO_2$ to long-chain hydrocarbons, and much attention has been paid on the improvement of these catalysts during the last years [17–19]. Combining the LTCPO of methane with an advanced Fischer–Tropsch synthesis could therefore result in an
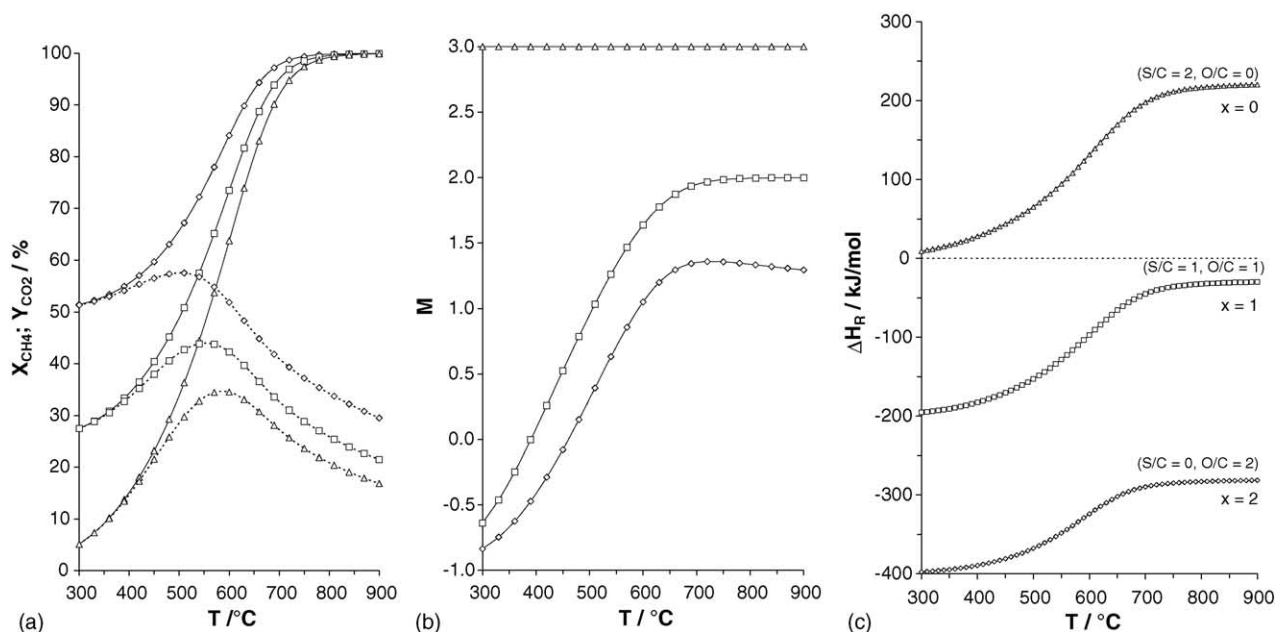


Fig. 1. Calculation of (a) methane conversions ($X_{CH_4}$, solid lines) and $CO_2$ yields ($Y_{CO_2}$, broken lines), (b) $M$ factor and (c) reaction enthalpy according to Eq. (1) with $x = 0, 1, 2$ and $y = 0$ as input composition. Symbols: ($\diamond$) $x = 2$, ($\square$) $x = 1$, and ($\triangle$) $x = 0$. $p = 0.1$ MPa. All calculations were performed with the Aspen Plus program package.