



# Catalytic partial oxidation of methane over nickel and ruthenium based catalysts under low $O_2/CH_4$ ratios and with addition of steam



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## HIGHLIGHTS

- Ni and Ru catalysts were tested at low  $O_2/CH_4$  ratios and in the presence of steam.
- The metallic surface area of the catalysts influenced the temperature profile.
- Catalyst deactivation by carbon formation was examined.
- The ruthenium catalyst did not formed appreciable amounts of carbon.

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## ABSTRACT

Catalytic partial oxidation (CPO) of methane to synthesis gas at low  $O_2/CH_4$  ratios and in the presence of steam was investigated over nickel and ruthenium catalysts supported on hydrotalcite-derived materials. The influence of catalyst properties and composition on activity, temperature profile and deactivation by carbon formation was examined. All catalyst presented high methane conversions, close to the values predicted by thermodynamic equilibrium and such conversions increased in proportion to the metal surface of the catalyst tested. The temperature profiles at  $O_2/CH_4 = 0.2$  and  $H_2O/CH_4 = 0.3$  and a constant exit temperature of 700 °C varied depending on the catalyst type; it was possible to examine catalyst deactivation from the change in the shape of the profile of each catalyst. Since the  $O_2/CH_4$  and  $H_2O/CH_4$  ratios were low, the risk or potential for carbon formation was thermodynamically favorable along the entire catalytic bed; however, this potential was qualitatively higher when the temperature profile of the catalyst presented a pronounced maximum peak at the inlet of the reactor. During catalytic reaction tests and methane decomposition experiments, the ruthenium catalyst did not formed appreciable amounts of carbon while a bimetallic catalyst (Ni and Ru) form only small amounts (in comparison with the nickel catalysts). For the ruthenium catalyst, a higher  $O_2/CH_4$  ratio favored conversions closer to the equilibrium value. The observations presented in this work indicate that during the CPO of methane, at low  $O_2/CH_4$  ratios and in the presence of steam, the catalyst properties and composition will have a substantial influence on the extent of the combustion and reforming reactions along the catalytic bed. This will in turn define the temperature profile, and therefore the risk or potential for carbon formation; this risk might effectively be overcome by the use of ruthenium-containing catalysts.

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## 1. Introduction

Natural gas plays an increasing strategic role in the global markets of power generation, space heating, transportation fuels and petrochemicals [1]. Proven reserves of conventional gas reach around 6800 TCF, of which about 40% are considered “stranded”

natural gas [2]. Furthermore, new developments in horizontal drilling, in combination with hydraulic fracturing, have expanded the ability to recover unconventional natural gas (e.g. shale gas) [3]. A major step in the conversion of natural gas to chemical products (ammonia, methanol, dimethyl ether, synthetic fuels, etc.) is the production of synthesis gas. Although synthesis gas production from natural gas is highly efficient (in terms of carbon and energy efficiency), it is capital intensive and may be responsible for approximately 60% of the investments of large-scale gas conversion plants [4]. Therefore, there is great interest in optimizing process schemes and exploring new routes for syngas manufacture.

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New routes should take into account the requirements of the specific downstream process (e.g. syngas composition) as well as the proper manner of adaption to current process schemes. Emerging technologies such as catalytic partial oxidation (CPO) seem to be promising alternatives for natural gas conversion into synthesis gas; however, limiting aspects such as high oxygen consumption and potential safety issues are still obstacles for its adoption as a main reformer [5]. An alternative approach in order to use the CPO technology, in the context of an already commercial technology, is as a pre-reforming step in an autothermal reforming-based process [6].

In catalytic partial oxidation (CPO), the hydrocarbon feedstock and steam are mixed with oxygen to react in a catalytic bed to give synthesis gas. In general, it consists of a two-step process: both total and partial oxidation of methane followed by reforming and water-gas-shift reactions. This combined mechanism, at given inlet operating conditions, not only affects the product distribution, but might also influence the reactor temperature profile. For example, at moderately high oxygen contents (i.e.  $O_2/CH_4 = 0.5\text{--}0.6$ ), a hot spot even higher than  $1000\text{ }^\circ\text{C}$  was observed close to the inlet of the reactor; the addition of co-reactants ( $H_2O$  or  $CO_2$ ) might produce a reduction and/or movement of the hot spot downwards the catalytic bed [7–9]; additionally, it was reported that catalysts with enhanced thermal conductivity might reduce the hot spot and thus modify the temperature profile [10]. Although reaction conditions of a CPO reactor might be milder when used as a pre-reformer, there are still some considerations to take into account. For example, since oxygen is fed to the reactor, the catalyst in the first part of the catalytic bed might not be in metallic state and therefore several surface compositions of the catalyst could exist along the reactor [11,12]. Carbon deposition on the catalytic bed can also be an issue in a CPO pre-reformer since it will be operated at low steam-to-carbon and oxygen-to-carbon ratios. A recent work shows that in a system comprising an adiabatic CPO pre-reformer reactor followed by an autothermal reactor (ATR), there are several operating conditions at which the CPO can be operated in order to obtain a  $H_2/CO$  ratio of 2.0 at the exit of the ATR reactor [13]; however, the thermodynamic risk for carbon formation in the CPO pre-reformer could only be avoided by using an inlet stream with moderately high contents of oxygen and steam (approx.  $O_2/CH_4 > 0.45$  and  $H_2O/CH_4 > 0.35$ ); unfortunately, under these conditions, the hot spot may still be an issue. Fortunately, depending on the nature of the catalyst of the CPO pre-reformer, it could be possible to operate the reactor at more critical conditions for carbon formation than those predicted by thermodynamics, for example, by using noble metals, stable nickel-based catalysts, or promoted catalysts [14,15]. Early experimental results under CPO conditions showed that the relative rates of carbon deposition follow the order  $Ni > Pd > Rh > Ru > Ir = Pt$  [16]; in nickel-based catalysts, whisker and encapsulated forms of carbon were found after reaction [16,17]. Furthermore, it was found that the step sites of metal surfaces are the most active for the steam reforming reactions [18], but unfortunately, step sites are also the most active for carbon formation; additionally, it was demonstrated that (very) small nickel crystals result in higher resistance to carbon formation [4,19]. Also, an enhanced adsorption of steam can decrease the steady state activity of carbon, and therefore the risk of carbon formation [20]; also, it was reported that carbon formation may, in some extent, be reduced by using certain types of basic catalyst supports [21].

In this regard, hydrotalcites have been studied as precursors for catalyst supports since they lead to materials with high surface area, basic properties; they are thermally stable and generate catalysts with small metal particle sizes [14,15,22]. Basini et al. [23–25] have studied nickel and rhodium catalysts with different metal loadings and compositions of hydrotalcite-like supports; they reported that

low nickel-content catalysts showed higher resistance to carbon formation during the CPO reaction. Also, the work carried out by Takehira and co-workers [26,27] concluded that oxidation of nickel/hydrotalcite catalysts during steam reforming and partial oxidation of hydrocarbons can be suppressed by adding traces of noble metals which keep the nickel surface in the reduced state by hydrogen spillover from noble metals to nickel particles. Despite the high activity and stability of noble metals (which means small and/or high-capacity reforming reactors), a commercial-scale reactor would still require considerably large amounts of noble metal-based catalyst. Therefore, the use of less expensive metals, or at least, a reduced amount of noble metals, is preferable for catalyst preparation.

Although many studies have been published on the partial oxidation of methane with and without the addition of steam, just a few, to our best knowledge, deal with the behavior of the catalytic system under low  $O_2/CH_4$  ratios. Since ruthenium is one of the most active metals for both partial oxidation and steam reforming while nickel is fairly active, inexpensive and widely used for methane steam reforming, it seems reasonable to carry out a preliminary study including these metals. Also, due to the beneficial properties found in the use of hydrotalcite-derived materials as catalyst supports, it might also be worthwhile to employ them. Furthermore, in order to have an initial overview of the CPO process under low  $O_2/CH_4$  ratios and in the presence of steam, different catalyst properties must be taken into account and be related to the catalyst performance.

Therefore, the aim of this study is to demonstrate the influence of catalyst properties and composition on the catalytic activity, temperature profile and carbon formation over nickel and ruthenium catalysts supported on hydrotalcite-derived materials as well as a commercial nickel catalyst, at low  $O_2/CH_4$  ratios in the presence of steam. Furthermore, the catalytic performance of a selected catalyst was studied at different operating conditions.

## 2. Experimental

### 2.1. Catalyst preparation

The catalysts were prepared by incipient wetness (co-) impregnation using nitrate-based precursors of nickel and ruthenium,  $Ni(NO_3)_2 \cdot 6H_2O$  and  $RuNO(NO_3)_3$  (Alfa Aesar), respectively, and a commercial hydrotalcite-type material as support (Sasol Pural MG 30, aluminum magnesium hydroxy carbonate,  $MgO:Al_2O_3 \sim 30:70$ ). Prior to the impregnation procedure, the support was calcined in air ( $850\text{ }^\circ\text{C}$ , 5 h). After impregnation and drying ( $120\text{ }^\circ\text{C}$ , 3 h), the samples were calcined in air at  $400\text{ }^\circ\text{C}$  for 5 h. This calcination temperature was reported to be enough to decompose the nitrate precursors into metal oxides [28]. Also, this low temperature may help reduce the strong interaction between nickel and the support (Ni–Al and Ni–Al–Mg spinel species, which, once formed, are very difficult to reduce requiring temperatures higher than  $900\text{ }^\circ\text{C}$  for catalyst activation) [26,29,30]. The resulting catalysts had a metal loading of 15 wt% Ni, 5 wt% Ni – 0.3 wt% Ru, and 1 wt% Ru, respectively. In addition, a commercial nickel-based catalyst was included in this study. Although a comparison of catalysts with different metal loadings may be doubtful, the different properties exhibited by them were very useful and somehow sufficient for the present study. Hereinafter, these four catalysts are referred as 15Ni, 5Ni–03Ru, 1Ru, and Ni–Com.

### 2.2. Catalyst characterization

Nitrogen adsorption measurements of the calcined catalysts were performed at  $-196\text{ }^\circ\text{C}$  (77 K) in an Autosorb iQ unit

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