# Super-dry reforming of CH4

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## 1. Introduction

During the past decade, environmental research targeting the mitigation of  $CO_2$  emissions has been shifting from  $CO_2$  storage towards  $CO_2$  utilization. The conversion of  $CO_2$  to CO could provide a cheap  $C_1$  building block for the chemical industry. Development of processes for  $CO_2$  conversion are necessary to fully exploit these properties. In this respect, the conversion of diluted  $CO_2$  streams into CO by means of chemical looping is particularly interesting [1]. Among the chemical looping processes, super-dry reforming of  $CH_4$ takes up a prominent position as it allows for intensified  $CO_2$  utilization and can be driven by renewable energy sources such as biogas [2].

The super-dry reforming process (Figure 1) relies on the combination of a reforming catalyst, typically nickel based, with an oxygen carrier and CO<sub>2</sub> sorbent material, which are typically iron oxide and calcium oxide based. In the CH<sub>4</sub> oxidation step, a CO<sub>2</sub> rich mixture of CH<sub>4</sub> and CO<sub>2</sub> is dry reformed into syngas over the reforming catalyst. This syngas is fed to a mixed bed of oxygen carrier and CO<sub>2</sub> sorbent, where CO and H<sub>2</sub> are converted into CO<sub>2</sub> and H<sub>2</sub>O upon reduction of the oxygen carrier, while CO<sub>2</sub> is fixated by the CO<sub>2</sub> sorbent. In the CO<sub>2</sub> reduction step, the oxygen carrier and CO<sub>2</sub> sorbent materials are regenerated either by increasing temperature or isothermally by means of a sweep gas. A major advantage of this process is its potential to achieve a three times higher capacity for CO<sub>2</sub> conversion than conventional CH<sub>4</sub> dry reforming.

The oxygen carrier is the heart of the super-dry reforming process, periodically cycling between reduction by syngas and reoxidation by  $CO_2$ , thus allowing the conversion of  $CO_2$  into CO. Indeed, the choice of oxygen carrier material is governed by the degree of reducibility of the oxygen carrier and its capacity to convert  $CO_2$  into CO. The reforming catalyst aids in achieving deepest possible reduction of the oxygen carrier by first converting the fuel to syngas. The role of the  $CO_2$  sorbent in super-dry reforming is threefold: (i) A tremendous decrease in coke formation on the nickel catalyst can be achieved because a higher  $CO_2$ :CH<sub>4</sub> feed ratio can be used without compromising the product purity. (ii) The  $CO_2$  sorbent also enhances the reducibility of the oxygen carrier by a continuous in situ removal of  $CO_2$ . Hence, H<sub>2</sub>O is the main product during the first step of super-dry reforming, even though 4 different processes (dry reforming, WGS reaction, oxygen carrier reduction,  $CO_2$  removal) occur. (iii) In the  $CO_2$  reduction step of the super-dry reforming process, decomposition of the  $CO_2$  sorbent provides  $CO_2$  for the oxygen carrier reoxidation, hence producing CO.The aim of this work is to study the stability and activity of functional materials applied in super\_dry reforming.

#### 2. Experimental

As dry reforming catalyst, a nickel based material was prepared [3]. As oxygen carrier and  $CO_2$  sorbent, an iron oxide based [4] and calcium oxide [2] or lithium orthosilicate based material were prepared. Nanomorphology and chemical information were obtained by materials characterization via STEM-EDX. For studying solid phase transitions, time-resolved in situ XRD experiments were performed in a Bruker-AXS D8 Discover apparatus with Cu K $\alpha$  radiation and a Vantec linear detector. For studying the gas phase product yields, a quartz tube microreactor (inner diameter of 10mm) was used. The reactor, equipped with K-type thermocouples contacting the reactor walls at the position of the catalyst bed, was heated by an electric furnace. EkviCalc [5], a software package containing an extensive database of chemical species, was used for performing thermodynamic calculations.

#### 3. Results and discussion

By combining a Ni/MgAl<sub>2</sub>O<sub>4</sub> dry-reforming catalyst, Fe<sub>2</sub>O<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> oxygen carrier and CaO/Al<sub>2</sub>O<sub>3</sub> CO<sub>2</sub> sorbent in the isothermal super-dry reforming process, a higher CO production yield was obtained than through conventional dry reforming. The increased yield of CO can be explained through the inherent separation of H<sub>2</sub>O from CO, hence avoiding equilibrium limitations in CO yield caused by the water-gas shift reaction. In fact, this two-step process owes its success to the application of Le Chatelier's principle in both steps. In the CH<sub>4</sub> oxidation step, the reduction of iron oxide is improved by continuous removal of CO<sub>2</sub> in the form of CaCO<sub>3</sub>. In the CO<sub>2</sub> reduction step, the introduction of an inert sweep gas initiates the decomposition of CaCO<sub>3</sub> upon which the oxygen carrier is reoxidized by CO<sub>2</sub>. Here, the formation of CO provides a driving force towards the complete decomposition of CaCO<sub>3</sub>. Overall, the theoretical yield of super-dry reforming goes up to four molecules of CO per CH<sub>4</sub> with a space-time yield of 7.5 mmol<sub>CO</sub> s<sup>-1</sup> kg<sub>Fe</sub><sup>-1</sup> at 1023 K. [2]

The effect of the choice of materials (reforming catalyst, oxygen carrier and  $CO_2$  sorbent) and their cyclic stability are investigated. A major challenge in the design of the reforming catalyst is the mitigation of catalyst deactivation through carbon deposits. One promising strategy is the addition of iron to obtain a Ni-Fe/MgAl<sub>2</sub>O<sub>4</sub> catalyst, in which iron assists in the oxidation and removal of carbon deposits from the catalyst surface [3]. The long-term application of an oxygen carrier is mostly limited by sintering and the undesired formation of inactive solid phases. To this end,  $50Fe_2O_3/MgAl_2O_4$  seems to provide a good candidate in terms of material stability and activity based on cyclic redox experiments over 4 days time on stream. As for the CO<sub>2</sub> sorbents, CaO based and Li<sub>4</sub>SiO<sub>4</sub> based materials are compared. One possible strategy for increasing the cyclic stability of the CO<sub>2</sub> sorbent is the application of a coating, such as  $ZrO_2$  (Figure 2). The aim of doing so is to reduce the effect of crystallite growth due to sintering by providing a physical barrier between the different CO<sub>2</sub> sorbent particles. However, it needs to be addressed whether or not this coating has any adverse effect on the properties of the CO<sub>2</sub> sorbent material, such as a reduced accessibility of the core material for CO<sub>2</sub>. Hereto, both experimental evidence and thermodynamic considerations are taken into account.

### 4. Summary

This work discusses the material properties, important for the real-life implementation of the super-dry reforming process. On the one hand, the properties of a structured  $CO_2$  sorbent material, based on Li<sub>4</sub>SiO<sub>4</sub> and ZrO<sub>2</sub>, are investigated in view of its application. On the other hand, the effect of redox cycling on different Fe<sub>2</sub>O<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> oxygen carrier materials is elaborated on.

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Figure 1 Schematics of the super-dry reforming process



**Figure 2 STEM-EDX characterization of Li<sub>4</sub>SiO<sub>4</sub>-ZrO<sub>2</sub> CO<sub>2</sub> sorbent material.** (A) EDX elemental mapping of Zr and Si, clearly showing the presence of a silica based particle, coated by zirconia. (B) Corresponding HAADF-STEM image. Scale bar represents 100 nm.