Syngas Production via Chemical Looping Partial Oxidation

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Introduction
Recent advances in drilling technology have dramatically increased the available natural gas reserves in North America. This has initiated renewed interest in the utilization of natural gas in the energy sector and chemical industry. Beyond combustion, natural gas can be utilized to produce wide range of chemicals and intermediates, but any such conversion currently requires conversion of methane to syngas (H2 and CO) in a first step.

Syngas is industrially produced by steam reforming of methane. However, SMR is a highly endothermic process, which requires further gas clean-up steps (such as water gas shift (WGS), CO2 removal and methanation) to achieve the desired syngas ratio of H2/CO = 2 for typical downstream processes. Hence, Catalytic Partial Oxidation of Methane (CPOM) has received much attention as alternate process in recent years. In CPOM, methane is converted with molecular oxygen over noble metal catalysts via CH4 + ½ O2 = 2 H2 + CO.1 Due to exothermic nature of the reaction, the process can be operated autothermally at temperatures well in excess of 1000°C, resulting in fast turnover rates and highly compact reactors.2,3 Moreover, the exothermicity of the reaction eliminates the parasitic energy load of external firing required in endothermic SRM. Despite the obvious advantages of CPOM, however, no major industrial CPOM process has been built to-date, largely due to concerns over handling CH4/oxygen mixtures at very high temperature near the upper flammability limit. Moreover, CPOM requires a pure oxygen feed to avoid dilution of syngas by N2 if air is used as oxidant.

Here, we are introducing chemical looping partial oxidation of methane (CLPOM) as a novel route for syngas production which avoids these major drawbacks of CPOM: Like chemical looping combustion, CLPOM relies on the periodic oxidation of a carrier materials with air and its reduction in contact with methane. However, unlike CLC, we aim to control the degree of carrier oxidation and reduction such that instead of complete combustion only incomplete, i.e. partial oxidation of methane occurs. In the present contribution, we show proof-of-concept results for CLPOM in a fixed-bed reactor configuration using Ni-, Fe-, and FeNi-based carrier materials.

Materials and Methods
Support materials were either synthesized in our lab (ceria) or obtained commercially (alumina). Metals were deposited via wet impregnation or deposition precipitation to obtain 40wt% metal loadings. Bimetallic carriers were synthesized with Fe:Ni = 2. The obtained powders were calcined and then characterized by TEM, BET and XRD.

The oxygen carriers (100 mg) were then tested for CLPOM in a fixed-bed reactor. Methane diluted in argon (16.7% CH4 in Ar, 1 sccm) was passed over the carrier bed and the reactor effluent was analyzed via mass spectrometry (Pfeiffer Omnistar QMS200) to monitor fuel conversion and product composition. Tests were conducted at ambient pressure over a temperature range of 700-900°C.

Results and Discussion
We find that all carriers undergo three subsequent processes for methane oxidation during exposure to the reducing environment of methane in CLPOM tests, as illustrated in figure 1, using Fe-CeO2 as example. During the initial period of reduction, all carriers show activity for total oxidation (indicated by the formation of large amounts of CO2) due to the large amount of oxygen available initially. Due to continuous depletion of oxygen during reduction, the selectivity for CO2 drops off and the concurrent rise in H2 and CO selectivity indicates the onset of partial oxidation of methane with a peak selectivity of ~80% for CO in case of Fe-CeO2. Once the oxygen carrier is almost completely reduced, the reaction pathway finally switches to methane cracking on the reduced metal. This sharp variation in CO2 and CO selectivity as a function of oxidation state of the oxygen carrier during reduction validates and highlights the principle of CLPOM: By controlling the oxygen available in the carrier, methane can be selectively oxidized to produce syngas as illustrated by the high syngas selectivity during the FeO -> Fe transition, while total oxidation dominates during the Fe2O3 -> Fe3O4 transition. By controlling the residence time of the carriers in the reduction and (re-)oxidation half cycles, respectively, or, in case of fixed bed reactors, by controlling the duration of the respective half-cycles, the carrier can hence be cycled between appropriate oxidation states to achieve high methane conversion with good syngas selectivity.

Our results furthermore show that Ni is more active than Fe but less selective for partial oxidation, and that by using bimetallic FeNi carrier materials one can achieve a compromise between the activity and selectivity of both metals.

![Figure 1. Selectivity of methane conversion towards partial and total oxidation products during a single reduction half cycle in CLPOM fixed-bed reactor operation with a 40wt% Fe-CeO2 carrier at 800°C and ambient pressure. Selectivity is shown vs carrier conversion (which is a function of time).](image)

Significance
CLPOM is an attractive novel process variant for efficient and safe conversion of methane to synthesis gas using low-cost transition metals and air as oxidants. The present results constitute the first proof-of-principle for this concept and present a set of materials which can serve as enablers for this process.

References