

CHEMICAL LOOPING DRY REFORMING: CO₂ AS A “SOFT” OXIDANT FOR SYNGAS PRODUCTION

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Abstract

Chemical Looping Combustion is a clean combustion technology for fossil or renewable fuels. In the current work we demonstrate that the application of so-called “chemical looping” scheme—the periodic oxidation and reduction of a metal oxide carrier to couple two independent redox reactions—to the activation of CO₂ via reduction to CO and the simultaneous production of synthesis gas (CO+ H₂) from CH₄. Two different operation modes are investigated and compared: In one scheme, the high reactivity of Fe for CO₂ reduction is coupled with the excellent reactivity of Ni for CH₄ activation—either in a bimetallic carrier or a simple physical mixture—to produce separate CO and syngas product streams. In a second operation mode, monometallic Ni carriers are utilized to produce completely separated CO and H₂ product streams. The process configurations demonstrate the potential of CO₂ as a “soft” oxidant which enables selective oxidation reactions via novel, intensified chemical looping processes with improved safety, capital costs and efficiency.

Keywords

Chemical looping, dry reforming, soft oxidant

Introduction

The recent surge in natural gas production has renewed interest in utilizing this resource for production of chemicals and liquid fuels. Despite extensive research, direct conversion of methane to chemicals remains elusive to-date and any industrial route for methane upgrading requires conversion to synthesis gas or “syngas”, a mixture of CO and H₂, followed by further conversion processes, such as Fischer-Tropsch or methanol synthesis. Currently, syngas is primarily produced via steam reforming of methane (CH₄ + H₂O = CO + 3 H₂; SRM), which stoichiometrically yields a syngas ratio of H₂:CO = 3 and hence requires further downstream processing (incl. water gas shift, CO₂ removal, and/or methanation) to adjust the H₂:CO ratio to the desired value required for the respective downstream process (typically H₂:CO = 2).

Chemical looping combustion (CLC) is a rapidly emerging technology for clean combustion of fossil fuels. In CLC, a fuel is combusted in a “reducer reactor” in contact with an oxygen carrier (typically a transition metal oxide). The reduced metal oxide is then transferred to an “oxidizer reactor” for regeneration with air, and then

transferred back to the reducer, closing the materials ‘loop’. Previous work in our laboratory has shown that the chemical looping concept can be steered towards selective oxidation, i.e. production of the partial oxidation product syngas, via appropriate tailoring of the metal oxide and operating conditions (Bhavsar et al., 2013). Like the conventional partial oxidation process, this chemical looping partial oxidation process (CLPOM) yields syngas with H₂:CO at the preferred ratio (i.e. 2:1). However, unlike the conventional process, CLPOM entirely avoids explosive mixtures, does not need external air separation, and uses cheap transition metals.

As a further extension of this work we present chemical looping dry reforming (CLDR) as an alternative configuration for syngas production which additionally enables CO₂ utilization (via activation to CO) by replacing air with CO₂ as oxidant. Finally, by further tuning the operating conditions, a new process can be achieved in which the production of CO (from reduction of CO₂) is coupled with the production of a separate, ultra-pure hydrogen stream from methane cracking.

Results

Briefly, supported metal oxide carriers were synthesized by a simple wet impregnation technique (from nitrate precursors), characterized (XRD, SEM-EDAM, TEM) and tested in a thermogravimetric analyzer (TGA) and a fixed bed reactor set-up (coupled with a mass spectrometer).

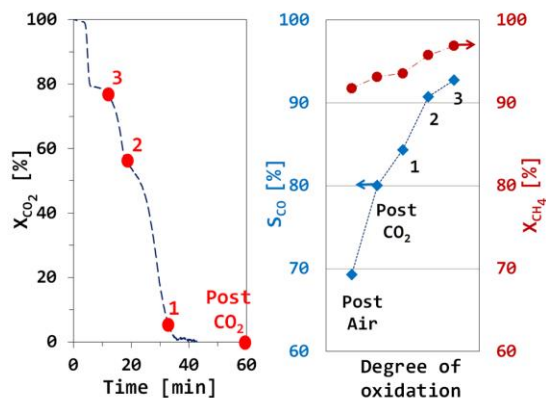


Figure 1: Concentration profiles during re-oxidation with CO₂. The inset shows CO selectivity and methane conversion during reduction with methane. (Bimetallic FeNi carrier, fixed bed reactor, T= 1000°C)

Figure 1 shows the oxidation of a reduced bimetallic FeNi (~10%Ni) carrier with CO₂ in a fixed bed reactor vs time. Production of CO is observed until CO₂ breakthrough occurs indicating complete oxidation. Carrier (re-)oxidation occurs in a step-wise manner (marked by 3 characteristic points). The inset shows the selectivity towards syngas (represented by CO) upon stopping the previous oxidation at various point (1-3) and on complete oxidation with air and CO₂, respectively. Syngas selectivity after complete oxidation with CO₂ is significantly higher than with air (80 vs 70%) reflecting the role of CO₂ as a “soft oxidant” for the carrier material. Interestingly, controlling the carrier oxidation further by stopping at earlier oxidation times (denoted by the numbers) results in further strong improvement in syngas selectivity with simultaneous improvement in CH₄ conversion. This indicates that selectivity is limited at higher oxidation states by sequential reaction (oxidation) of the primary oxidation product syngas, thus limiting the amount of oxygen available for oxidation of methane and hence limiting methane conversion. Overall, CO₂ thus allows for finely controlled oxidation of the carrier, enabling syngas selectivities and methane conversions well in excess of 90% in a simple process using cheap transition metals.

Interestingly comparing the behavior of a bimetallic FeNi carrier with a physical mixture of monometallic Fe and Ni carriers (at the same molar metal ratio; not shown here) reveals an intriguing cooperative reaction mechanism, where methane cracks over Ni carriers (which cannot be oxidized with CO₂) and the resulting H₂ is then oxidized in a (very fast) reaction with FeO_x. H₂O produced in this step then gasifies the carbon deposit on Ni, producing syngas as final product. Again this—highly efficient and simple—process is enabled by

the use of CO₂ as “soft” oxidant, since CO₂ cannot oxidize Ni and hence avoids the detrimental total oxidation catalyzed by NiO, as apparent from the results in figure 2: With increasing Ni content, syngas selectivity drops precipitously for air oxidation, while oxidation with CO₂ results in unchanged selectivity (due to its inability to oxidize Ni). Overall, CO₂ thus maintains the metallic state of Ni while oxidizing Fe and hence enables the combination of the high reactivity of Ni with the excellent selectivity of Fe through a gas-phase coupled cooperative reaction mechanism.

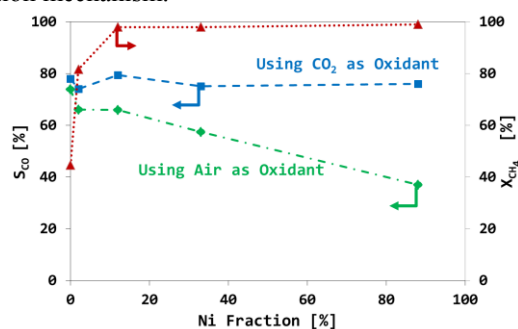


Figure 2: CH₄ conversion and syngas selectivity for Fe + Ni physical mixtures in a fixed bed reactor vs Ni fraction in the bed. Results for both air and CO₂ as oxidant are shown.

Finally, by removing the Fe carrier and operating with a monometallic Ni bed, an entirely new process is obtained in which the Ni carrier, in the absence of an oxygen source, catalyzes CH₄ cracking producing ultra-pure H₂ streams without the need for any further purification. The resulting carbon deposit (from the cracking reaction) is then removed during oxidation with CO₂—producing pure CO—without oxidizing the Ni phase. By suitable optimization of operating conditions, stable operation with conversions of CH₄ and CO₂ well in excess of 90% can be obtained.

Conclusions

Overall, our results demonstrate the use of CO₂ as a soft oxidant which enables controlled oxidation of an oxygen carrier and hence highly selective oxidation of methane to syngas in a family of flexible chemical looping processes. We expect that this reaction principle is extensible onto higher hydrocarbons, which is the target of on-going studies in our laboratory.

Acknowledgments:

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References

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