CO$_2$ conversion to CO by auto-thermal catalyst-assisted chemical looping

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A B S T R A C T

A bifunctional 9 wt.%NiO-16 wt.%Fe$_2$O$_3$/MgAl$_2$O$_4$ material was prepared for CO$_2$ conversion to CO by auto-thermal catalyst-assisted chemical looping. This process is designed to maximize CO$_2$ conversion. The generation of CO from CO$_2$ was investigated between 873 K and 1023 K. The high endothermicity of methane dry reforming and the material deactivation by coke deposition were avoided by the simultaneous feeding of CH$_4$, CO$_2$ and O$_2$ in a 1:1:0.5 molar ratio during the reduction half-cycle of chemical looping. In this half-cycle, interaction of Ni with Fe leads to Ni-Fe alloy formation. The resulting Ni-based catalyst converts CH$_4$ + CO$_2$ + O$_2$ into a mixture of CO and H$_2$, which both reduce Fe$_3$O$_4$, producing CO$_2$ and H$_2$O. In the CO$_2$ re-oxidation half-cycle, CO is produced and the Ni-Fe alloy decomposes into Ni and Fe$_3$O$_4$. The reduction capacity (R_c) of the gas mixture strongly depends on the ratio R_c between reducing and oxidizing gases. Based on thermodynamic calculations, high conversion of Fe$_3$O$_4$ to reduced state can be reached if $R_c > 2$ and $T > 873$ K. During prolonged auto-thermal chemical looping at 1023 K, the 9 wt.%NiO–16 wt.%Fe$_2$O$_3$/MgAl$_2$O$_4$ suffers from deactivation in the first five cycles, after which a more stable operation is established. Based on TEM measurements, sintering was found to be the main cause for the initial decrease of CO production.
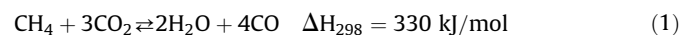
1. Introduction

World markets for liquid and gas fuels have entered a period of dynamic change—in both supply and demand [1]. Sustainable energy represents the most important scientific and technical challenge of the 21st century and will play a major role in the near future [2]. To date, fossil fuels are the world's major source of energy and as such the driving force behind human prosperity. Considering the depletion of fossil fuels due to continuously increasing energy demands, there is a growing need to investigate more efficient utilization of available resources including natural gas reserves [3]. Among the most widely studied technologies for conversion of CH$_4$ to mixtures of H$_2$ and CO are various reforming techniques such as steam reforming, dry reforming, partial oxidation and auto-thermal reforming [4–9]. These techniques differ in the oxidant used, the final H$_2$/CO product ratio, as well as the kinetics and energetics of the reaction. Dry reforming in particular utilizes two abundantly available greenhouse gases CH$_4$

and CO$_2$, to produce the industrially important syngas [10–14]. This process could constitute a viable first step towards efficient CO$_2$ capture and utilization.

As an alternative to conventional technologies, CH$_4$ reforming based on chemical looping is a process, designed to convert hydrocarbons to H$_2$ and CO [12,13,15–22]. Chemical looping is one of emerging technological options applicable in a diverse range of processes for production of fuels, chemicals, electricity, and in energy storage [17,23–26]. In a chemical looping process, a reaction is divided into sub-reactions. The link between the sub-reactions is a solid mediator, typically in the form of a metal oxide (e.g. Fe$_3$O$_4$, CeO$_2$, NiO and CuO) [17,18,27–30], which is reduced and re-oxidized in a cyclic progression of the sub-reactions.

For chemical looping methane dry reforming, the feed consists of CH$_4$ and CO$_2$. Methane reduces the metal oxide to metal during the first step and produces CO$_2$ and H$_2$O. In the second step, CO$_2$ is used as an oxidizing agent, thereby producing CO[18,19]. The overall reaction is the endothermic carbon dioxide reforming of CH$_4$ into CO:

$$CH_4 + 3CO_2 \rightleftarrows 2H_2O + 4CO \quad \Delta H_{298} = 330 \text{ kJ/mol} \tag{1}$$

Compared to dry reforming, this process utilizes more CO_2 than it produces in the reduction step. In the case of using CH_4 as reducing gas, the process can convert four times as much CO_2 than is produced.

The present chemical looping methane dry reforming process can be further designed to maximize CO_2 conversion to CO, CO being a highly reactive molecule, which is widely used in the chemical industry. The CO production by chemical looping is limited by the achieved degree of reduction of the metal oxide in the presence of H_2O and/or CO_2 [31,32]. The natural mixture of CH_4 with CO_2 significantly decreases the reduction rate of metal oxides because CO_2 also acts as an oxidizing agent. Both CO_2 in the feed and product have this retarding effect on the metal oxide reduction rate. This limitation can be overcome if a physical mixture of a Ni-based catalyst and iron oxide [33] or a bifunctional material [19,34] is used as oxygen storage material. During the first step, a mixed feed of CH_4 and CO_2 is then converted over the catalyst into syngas:

$$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2 \tag{2}$$
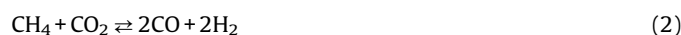
Both CO and H_2 then reduce the iron oxide:

$$4CO + Fe_3O_4 \rightleftarrows 4CO_2 + 3Fe \tag{3}$$

$$4H_2 + Fe_3O_4 \rightleftarrows 4H_2O + 3Fe \tag{4}$$

The importance of the Ni catalyzed CH_4 reforming process is stressed here since the reduction of iron oxide by H_2 and CO is considerably faster than by CH_4 [35,36].

The complete process with bifunctional mediator yields chemical looping CH_4 dry reforming as overall reaction, being a strongly endothermic process (Eq. (1)). Alternatively, the process could be rendered auto-thermal by co-feeding oxygen in close analogy to industrial auto-thermal CH_4 reforming [5,18].

$$CH_4 + xCO_2 + (3 - x)/2O_2 \rightleftarrows (1 + x)CO + 2H_2O \tag{5}$$
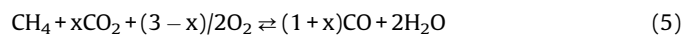
In chemical looping processes, several alternative schemes for oxygen co-feeding are possible [16,37–39]. The oxygen could be directly co-fed with CO_2 to the oxidizer, or it could be fed with CH_4 and CO_2 to the reducer. The latter option reduces the strong endothermicity of the reduction reaction.

Auto-thermal catalyst-assisted chemical looping is proposed here as a new process for CO production from natural gas. The process combines two strategies: CO production by chemical looping over Fe_3O_4 and auto-thermal catalytic conversion of CH_4, O_2 and CO_2 to syngas over a Ni-based catalyst. Auto-thermal catalyst-assisted chemical looping for the transformation of CO_2 to CO was investigated using a bifunctional $NiO-Fe_2O_3/MgAl_2O_4$ sample. Experimental performance data as well as structural characterization of the material during the reduction and re-oxidation are reported. The thermodynamic feasibility of an auto-thermal catalyst-assisted chemical looping process is studied.

2. Experimental

2.1. Materials preparation

$MgAl_2O_4$ support material was prepared by co-precipitation from an aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$ (99%, Sigma-Aldrich) and $Al(NO_3)_3 \cdot 9H_2O$ (98.5%, Sigma-Aldrich) (molar ratio Mg: Al = 1:2). A precipitating agent, NH_4OH (ACS reagent, 28.0–30.0% NH_3 basis), was added to adjust the pH to 10, at 333 K. The produced precipitate was filtered, dried at 393 K for 14 h, and subsequently calcined in air at 1023 K for 6 h. A $Ni-Fe/MgAl_2O_4$ catalyst was prepared by incipient wetness impregnation using an aqueous solution of corresponding nitrates $Ni(NO_3)_2 \cdot 6H_2O$

$(99.99+\%$, Sigma-Aldrich) and $Fe(NO_3)_3 \cdot 9H_2O$ $(99.99+\%$, Sigma-Aldrich). The catalyst was dried at 393 K for 12 h and subsequently calcined in air at 1023 K for 4 h. The Fe/Ni molar ratio was 1.6.

2.2. Characterization

The bulk chemical compositions of support and as prepared materials were determined by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICAP 6500, Thermo Scientific). The samples were mineralized by alkaline fusion with a mix of Li-tetraborate and Li-metaborate. The Brunauer-Emmett-Teller (BET) surface area of the samples was determined by N_2 adsorption at 77 K (five point BET method using Gemini Micromeritics). Prior to analysis the samples were outgassed at 573 K for 12 h to eliminate volatile adsorbates from the surface. The crystallographic phase of the as prepared material was determined using a Siemens Diffractometer Kristalloflex D5000, with Cu Kα radiation. The powder XRD pattern was collected in a 2θ range from 10° to 75° with a step of 0.02° and 30 s counting time per angle. By fitting a Gaussian function to a diffraction peak, the crystallite size was determined from the peak width via the Scherrer equation, while the peak position gave information about the lattice spacing based on the Bragg law of diffraction: $2d\sin(\theta) = n\lambda$ [40]. A more detailed characterization of the $Ni-Fe/MgAl_2O_4$ can be found in a previous work [41].

2.3. In-situ time resolved XRD

In-situ XRD experiments were performed in a home-built reaction chamber incorporated inside a Bruker-AXS D8 Discover apparatus (Cu Kα radiation of 0.154 nm). The chamber had a Kapton foil window for X-ray transmission. The setup was equipped with a linear detector covering a range of 20° in 2θ with an angular resolution of 0.1°. The acquisition time of XRD patterns was 10 s. A K-type thermocouple was used for temperature measurements and corrected afterwards to a calibration curve of the heating device. Approximately 10 mg of powdered sample was evenly spread on a single crystal Si wafer. Interaction of the catalyst material with the Si wafer was never observed. Prior to each experiment, the reactor chamber was evacuated to a base pressure of 4 Pa by a rotation pump. Gases were supplied to the reactor chamber from a rig with calibrated mass-flow controllers.

The evolution of the catalyst crystallographic structure during H_2-TPR, CO_2-TPO and isothermal CH_4 dry reforming (DRM) was examined. For temperature programmed experiments, the sample was heated from room temperature to 1123 K, using a heating rate of 30 K/min under the flow of 1 ml/s of 10% H_2/He or CO_2 respectively. During reaction experiments, the sample was first reduced (1 ml/s of 10% H_2/He) at 1023 K before DRM reaction. A full XRD scan (10° to 65° with a step of 0.02°) at room temperature was taken before and after each TPR, TPO and DRM reaction experiment.

2.4. Reactor setup and procedures

Activity measurements were carried out at atmospheric pressure in a quartz tube microreactor (i.d. 10 mm), placed in an electric furnace. Typically, 100 mg of sample was packed between quartz wool plugs. The samples were diluted with quartz in a 1:5 mass ratio. The temperature of the bed was measured with K-type thermocouples touching the outside and inside of the reactor at the position of the catalyst bed.

The activity during normal CH_4 dry reforming was measured from 373 K till 1123 K. First the sample was reduced in a 1.1 mL/s flow of 10%H_2/He at 923 K for 10 min and then the flow was switched to He. After this step, a mixture with $CH_4:CO_2:O_2:$He