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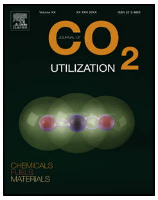

CO production from CO_2 via reverse water–gas shift reaction performed in a chemical looping mode: Kinetics on modified iron oxide

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ABSTRACT

Carbon monoxide production from carbon dioxide via isothermal reverse water–gas shift chemical looping (RWGS-CL) is studied with a modified iron oxide oxygen carrier material (80 wt% Fe_2O_3–$Ce_{0.5}Zr_{0.5}O_2$). The material is characterized by TEM, XRD and thermogravimetry at temperatures from 750 °C to 850 °C and gas mole fractions of H_2 and CO_2 from 0.05 to 0.75, respectively. High temperature and high reactant concentrations favor the oxidation and reduction of the material during repeated redox cycles. The reaction rate of reduction is always faster than that of oxidation applying the same gas concentration of H_2 and CO_2, respectively. The long term stability of the material is investigated with 500 redox cycles in a plug flow reactor. The material shows gradual deactivation lowering the CO yield during the first 100 redox cycles. After that, a steady state CO yield is reached for the next 400 redox cycles. Deactivation is attributed to surface sintering which results in slower reaction kinetics. TG data was used for a kinetic analysis applying the master plot method. The experimental data for oxidation and reduction indicated reaction mechanisms, which are well described by a reaction order and a geometrical contraction model. After parameter estimation, a good agreement between the model and the TG data was achieved with the reaction order and geometrical contraction model for oxidation and reduction, respectively. The RWGS-CL process can be used for sustainable CO production from CO_2 if the energy for the process and for H_2 production is supplied by renewable sources.

1. Introduction

The Intergovernmental Panel on Climate Change stated in their most recent report [1] that the human influence on climate change is unequivocal. The rapid rise of anthropologically generated CO_2 within the last decades and its effect on global warming necessitate the development of carbon-neutral processes to close the carbon cycle. However, because of its low reactivity CO_2 has few applications in industry and is often exhausted into the atmosphere. Finding ways to use the massive amounts of CO_2 produced every year makes processes greener and might be economically and environmentally beneficial [2,3].

In recent years, research on (thermo-)chemical looping processes has increased substantially with chemical looping combustion as the main research area for inherent CO_2 separation and capture. Thermochemical looping has been shown to be a viable process for the production of CO, H_2 or a mixture of both (syngas) by splitting CO_2 or water in a cyclic process applying a solid oxygen storage material (OSM) [4,5]. It has been estimated that thermochemical processes have the highest present and future sun-to-fuel (STF) efficiency [6] for the conversion of CO_2 from fossil power plants to sustainable fuels. However, temperatures exceeding 1000 °C are typically needed for the thermal reduction of the OSM, resulting in energy intensive processes and challenging material handling. Milder conditions can be applied by using reducing agents (e.g. H_2 or CH_4) for the reduction of the material [4]. Introducing H_2 for material reduction leads to the reverse water-gas shift chemical looping (RWGS-CL) process, which was investigated by Galvita et al. [7,8] and Daza et al. [9]. It is the chemical looping equivalent of the conventional reverse water-gas shift (RWGS) reaction, in which H_2 and CO_2 react according to Eq. (1).

$$H_2 + CO_2 \rightleftharpoons H_2O + CO \tag{1}$$

In this work, a mixed oxide of 80 wt% Fe_2O_3 and 20 wt% $Ce_{0.5}Zr_{0.5}O_2$ was used as OSM for RWGS-CL. In a previous study regarding the optimal composition of Fe_2O_3–$Ce_{0.5}Zr_{0.5}O_2$ for H_2

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Nomenclature

Abbreviations

MS	mass spectrometry
OSM	oxygen storage material
TG	thermogravimetry
XRD	X-ray diffraction

Symbols

α	reaction extent (–)
ν	stoichiometric coefficient (–)
θ	measurement angle in XRD (°)
Θ	generalized time (s)
$c_{t,g}$	total gas concentration (g/mol)
E_A	activation energy (kJ/mol)
f_i	model prediction values (–)
$\dot{F}$	volumetric gas flow rate (ml/min)
k	kinetic parameter (mol/kg s)
k^0	factor in Arrhenius equation (mol/kg s)
m_O,m_R	reaction order parameters (solid phase) (–)
m_j	mass of component j (g)
m_{OSM}	mass of the OSM (g)
M_{OSM}	molar mass of the OSM (g/mol)
n_O, n_R	reaction order parameter (gas phase) (–)
p	pressure (Pa)
r	reaction rate (mol/g s)
R	universal gas constant (kJ/mol K)
R^2	coefficient of determination (–)
t	time (s)
T	temperature (K)
V_{TG}	volume of thermogravimetry unit (ml)
w_i	mass fraction of component i (–)
x_i	mole fraction of component i (–)
y_i	observed experimental values (–)

production *via* chemical looping, Galvita et al. [10] concluded that a composition of 80 wt% Fe_2O_3 and 20 wt% $Ce_{0.5}Zr_{0.5}O_2$ led to the highest H_2 yield and good material stability. Although $Ce_{0.5}Zr_{0.5}O_2$ did not increase the oxygen capacity of the material, the supporting oxide was found to be of great importance, since it improves the structural properties compared to those of the pure Fe/Fe_3O_4 couple. ZrO_2 is known to increase the micro-structural stability against sintering [11], whereas CeO_2 increases material activity, enhancing the rate of reaction [7].

In the RWGS-CL process, two temporal stages can be identified: the reduction of the modified iron oxide with H_2 and subsequently its re-oxidization with CO_2 which yields the desired product, CO. The simplified reaction scheme (assuming that the support metal oxide, $Ce_{0.5}Zr_{0.5}O_2$, does not participate in the reactions) is given by Eqs. (2) and (3).

$$\text{Reduction}: \quad Fe_3O_4 + 4\,H_2 \rightleftharpoons 3\,Fe + 4\,H_2O \qquad (2)$$

$$\text{Oxidation}: \quad 3\,Fe + 4\,CO_2 \rightleftharpoons Fe_3O_4 + 4\,CO \qquad (3)$$

Redox reactions are considered to occur between Fe_3O_4 and Fe, since the fully oxidized state, Fe_2O_3, is not achievable by oxidation with CO_2 at the considered reaction conditions.

The main advantage of RWGS-CL compared to conventional RWGS is the inherent gas separation. Therefore, unwanted side reactions (e.g. methanation) are eliminated and product separation is simplified. In contrast to thermochemical looping, the RWGS-CL process can be operated isothermally, eliminating the need for solid-phase heat recuperation, which is crucial for process efficiency and economics [12]. Thus, reactor design and operation is simplified. Additionally, the oxygen storage capacity of the material can be exploited efficiently using H_2. While typical thermochemical cycles make use only of a small range in material non-stoichiometry (e.g. ceria-based) [13], here a much higher difference in oxidation state is achieved between the material's reduced and oxidized state. For the modified iron oxide used in this work (80 wt% Fe_2O_3 and 20 wt% $Ce_{0.5}Zr_{0.5}O_2$), the thermodynamically possible CO yield per cycle is 13.8 mol_{CO}/kg of Fe_3O_4–$Ce_{0.5}Zr_{0.5}O_2$ ($Ce_{0.5}Zr_{0.5}O_2$ is assumed to be inert). This is more than 20 times the amount that can be produced by using cerium oxide. A maximum CO yield of 0.58 mol_{CO}/kg_{CeO_2} is achievable assuming a cycle between CeO_2 and $CeO_{2-\delta}$ with a non-stoichiometry of $\delta = 0.1$. In the literature, CO yields of approximately 0.15 mol_{CO}/kg_{CeO_2} were reported for ceria [13] and 0.2–1.0 mol_{CO}/kg for state-of-the-art perovskite type materials [14,15]. All reported values here are normalized to the material mass in the highest achievable oxidation state in the corresponding redox cycle.

Current research on chemical looping is exploring materials with high oxygen capacity and structural stability over repeated cycling, like (doped or undoped) ceria and new types of perovskites, which show very promising results [9,16,17]. The modified iron oxide, as used in this work, is inexpensive but lacks structural stability at temperatures above approximately 1000 °C. However, since the temperature for RWGS-CL is lower than that of typical thermochemical looping processes, the use of modified iron oxide is justified.

In this work, the effect of repeated cycling on the crystallographic structure of the OSM is investigated *via* TEM and XRD. Further, a kinetic analysis of the modified iron material is provided as a basis for process design and analysis. A systematic methodology is applied to identify a kinetic model for the oxidation and reduction of the material, enabling the mathematical description of the process. Precise kinetic information available in the literature for various materials is still rather limited and often restricted to oxidation kinetics for thermochemical cycles [18–21]. To the best of our knowledge, there are as of yet no detailed kinetics reported for the RWGS-CL process.

2. Experimental

2.1. Material synthesis

The Fe_2O_3–$Ce_{0.5}Zr_{0.5}O_2$ samples were synthesized by urea hydrolysis using $Fe(NO_3)_3{\cdot}9H_2O$ (99.0%, Fluka), $Ce(NO_3)_3{\cdot}6H_2O$ (99.0%, Fluka) and $ZrO(NO_3)_3{\cdot}6H_2O$ (99.0%, Fluka). The mixed metal salt solution (0.1 M) was added to a 0.4 M solution of urea (99.0%, Fluka) to yield a salt to urea solution ratio of 2:1 (v/v). The precipitate solution was mixed at 100 °C for 24 h. After the suspension was cooled to room temperature, the precipitate was separated from the solution. The solid product was washed with ethanol and dried overnight in an oven at 110 °C. Finally, the prepared Fe_2O_3–$Ce_{0.5}Zr_{0.5}O_2$ was calcinated at 800 °C.

Since the synthesized, finely powdered material was unsuitable for a plug flow reactor (large pressure drop, high tendency towards sintering), the material was pelletized, crushed and sieved to obtain particles of a defined size between 260 and 520 μm.

2.2. Material pretreatment and stabilization

The aim of the experiments was to obtain kinetic information about the material. It is well known that the activity of oxygen storage materials decreases over repeated redox cycles [16,22]. The