Applied Energy 230 (2018) 696–711

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Enhanced performance of chemical looping combustion of methane by combining oxygen carriers via optimizing the stacking sequences

Xianming Cheng[a,b], Kongzhai Li[a,b,*], Xing Zhu[a], Yonggang Wei[a], Zhouhang Li[b], Yanhui Long[a,b], Min Zheng[a], Dong Tian[a], Hua Wang[a,b]

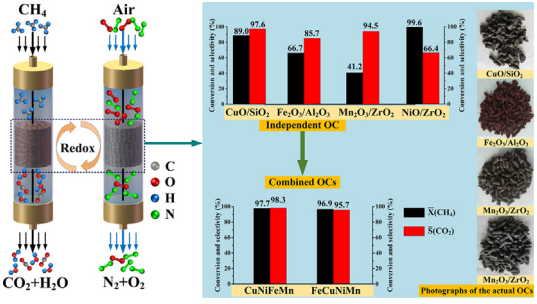
[a] State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming 650093, Yunnan, China
[b] Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, Yunnan, China

HIGHLIGHTS

- CuO/SiO_2, Fe_2O_3/Al_2O_3, Mn_2O_3/ZrO_2 and NiO/ZrO_2 OCs show complementarity for CLC of methane.
- CuO/SiO_2 OC in the combinations can effectively improve the CO_2 selectivity.
- NiO/ZrO_2 OC in the combinations is beneficial to the CH_4 conversion.
- Combined OCs with a stacking sequence of CuNiFeMn or FeCuNiMn effectively enhance the CLC performance.

GRAPHICAL ABSTRACT

In the present work, we propose a strategy for the first time to optimize the overall performance of the CLC system by combining different types of OC sticks in particular sequences. The synergy among different OCs can maximize the advantages and circumvent the weakness of the selected OCs. The combined OCs with CuNiFeMn or FeCuNiMn stacking sequence show both greatly enhanced activity for methane complete oxidation and superior resistance to carbon deposition. The average CH_4 conversion and CO_2 selectivity 97.3% and 98.3% for the CuNiFeMn sequence and 96.9% and 95.7% for FeCuNiMn sequence, respectively.



ARTICLE INFO

Keywords:
Chemical looping combustion
Activity
Redox stability
Combined oxygen carriers
Carbon deposition

ABSTRACT

Combination of different types of oxides is a general strategy to prepare high performance oxygen carriers (OCs) for chemical looping combustion (CLC) technology. However, the possible chemical interactions among different components during the long-term redox cycling may reduce the stability of OCs. In the present work, we physically combine different types of OC sticks (i.e., CuO/SiO_2, Fe_2O_3/Al_2O_3, Mn_2O_3/ZrO_2 and NiO/ZrO_2) in particular stacking sequences in a fixed bed reactor to improve the CLC performance. The reaction between methane and CuO is exothermic and the CuO/SiO_2 OC exhibits very high activity for methane oxidation and superior resistance to carbon deposition. It is suitable to place the CuO/SiO_2 in the front of the sequence which can sufficiently convert methane, and the heat releasing from this reaction will promote the following endothermic reactions. NiO/ZrO_2 OC also represents very high activity for CH_4 oxidation but results in serious carbon deposition. Since the reduced metallic Ni is an active catalyst for methane activation, it is suggested to place NiO/ZrO_2 in the middle of the sequence to enhance the further conversion of methane and to provide enough space to remove the carbon deposition via the gasification by CO_2 or H_2O generated from the front reaction. Mn_2O_3/ZrO_2 OC possesses poor activity for methane conversion but high resistance to carbon deposition, which can be used to convert unreacted methane in the end of the sequence. Fe_2O_3/Al_2O_3 OC is not an important issue due to the low activity and reaction rate. As a result, the combined OCs with a stacking sequence of CuNiFeMn or

* Corresponding author at: Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, Yunnan, China.
E-mail addresses: kongzhai.li@foxmail.com, kongzhai.li@aliyun.com (K. Li).

https://doi.org/10.1016/j.apenergy.2018.08.063
Received 22 May 2018; Received in revised form 31 July 2018; Accepted 15 August 2018

FeCuNiMn show high performance in CH_4 conversion (> 97%), CO_2 selectivity (> 96%), redox stability and resistance to carbon deposition. These results make a certain reference for using the combined OCs in the large-scale CLC system.

Nomenclature

Abbreviations

CCS	carbon capture and sequestration
CLC	chemical looping combustion
HSC	enthalpy (H), entropy (S) and heat capacity (C)
JCPDS	Joint Committee on Powder Diffraction Standards
H_2-TPR	temperature programmed reduction of hydrogen
CH_4-TPR	temperature programmed reduction of methane
NDIR	Nondispersive Infrared Radiation
$X(CH_4)$	CH_4 conversion
$\overline{X}(CH_4)$	average methane conversion
$S(CO_2)$	CO_2 selectivity
$\overline{S}(CO_2)$	average CO_2 selectivity
OSC	oxygen storage capacity
OC	oxygen carrier
XRD	X-ray diffraction
BET	Brunauer, Emmett and Teller
SEM	scanning electron microscopy

Symbols

ΔH_R	enthalpy of reaction, kJ/mol
C	concentration

Subscripts

in	inlet gas
out	outlet gas

1. Introduction

The rapid growth of the global economy results in the increasing demand for energy. Although new energy sources such as renewable energy and nuclear power have been in development, the limited applications make it far short of the demand for energy in modern society. Almost 80% supply of the world energy consumption in the near future will still strongly depend on traditional fossil fuels (coal, oil and natural gas) [1,2]. However, the combustion of fossil fuels will emit large amount of greenhouse gas (mainly CO_2) into the atmosphere, bringing the adverse effects on the environment. Therefore, it is of urgent necessity to decrease CO_2 emission from fossil fuel combustion to protect the environment from the greenhouse effect.

Among current and emerging technologies, Carbon Capture and Storage (CCS) can provide clean energy by capturing the carbon dioxide emissions produced from the combustion of fossil fuels in electricity generation and industrial processes, which could account for up to 19% of the total reduction in emissions needed according to the IPPC and IEA reports [3]. The main objective of CCS is to produce a high concentrated CO_2 stream that can be captured and subsequently kept in a suitable storage location for long time. However, the CCS technology will inevitably reduce energy efficiency with the increase in price of energy. In comparison to all these techniques related to CCS available with a great energy consumption and cost penalty, chemical looping combustion (CLC) is considered as the most efficient option with the lowest efficiency penalty for the inherent separation of CO_2 without any extra energy consumption [4,5].

In the CLC process, fuel reacts with a solid oxide (named oxygen carrier, OC) to produce CO_2 and H_2O, and then the reduced OC can be re-oxidized by air for cycling. In this way, oxygen is transferred from the air to the fuel via OCs. Water vapor can be easily removed by condensation to obtain pure CO_2, avoiding the consumption of extra energy for CO_2 separation in the conventional combustion. After the regeneration of the reduced OCs by air, a clean and high-temperature spent-air stream is generated for power production. The total enthalpy change evolved from the oxidation and reduction steps is the same to the conventional combustion. The energy penalty of the CLC process for CO_2 capture is extremely low because of the avoidance of expensive gas separation unit [2,6,7].

During the last decades, massive efforts have been made to develop appropriate OCs for the CLC system. For a large scale application, the most extensively investigated OCs in literatures to date are Ni- [3,5,8–10], Cu- [11–14], Fe- [15–20] and Mn-based OCs [21–25]. The most frequently employed inert supports include Al_2O_3, SiO_2, ZrO_2, TiO_2, bentonite, etc. These supports usually not react with fuels but expected to enhance the reactivity and dispersity of active oxides and improve the long-term stability of OCs [5]. For the selection of the support, the agglomeration and interactions between the active metal and the support may influence its performance.

In most of the used Ni-based oxygen carrier, Dueso et al. [26] and Gayán et al. [27] investigated the reactivity of NiO/Al_2O_3 in fluidized bed reaction and found that the formation of $NiAl_2O_4$ affected negatively to the OC reactivity and CO_2 selectivity during the reduction reaction. Corbella et al. [28] investigated the NiO/TiO_2 for CLC of methane and found that the formation of $NiTiO_3$ is a very stable compound, which reduces the oxygen carrying and causes poor reactivity compared to free NiO. Zafar et al. [29] suggested that NiO/SiO_2 prepared by dry impregnation showed very high reactivity at lower temperature but the reactivity decreased as a function of the cycle numbers at 1173 K. Mattisson et al. [30] and Adánez et al. [31] proposed that the NiO supported by ZrO_2 exhibited high reactivity and high degree of regenerability for the CLC process.

Cu-based OCs have high reactivity and oxygen carrying capacity, but the relatively low melting point of Cu usually cause the easily sintering in the reduction step at a high temperature, leading to a drastic degradation in the cycle performance. Adánez et al. [31] investigated reactivity of CuO/Al_2O_3 for CLC of methane in fluidized bed reactor and found that it has problems of agglomeration and the reactivity reduces drastically in the redox cycling due to the formation of $CuAl_2O_4$. Similarly, CuO/TiO_2 tends to form $CuTiO_4$ complex compound, which reduces its activity in long term CLC process [32]. The use of SiO_2 as support material for CuO is also investigated [33–35]. Digeo et al. evaluated the cycle performance of CuO/SiO_2 prepared by impregnation, and they observed that CuO/SiO_2 does not degrade substantially in 100 redox cycles [31,36].

Fe-based oxygen carrier is a nature abundant and cheap material, which has the potential to fully convert gaseous fuel into a stream of CO_2 and H_2O. For Fe-based OCs, SiO_2 is regarded as incompatible support material because of the generation of unreactive iron silicates [37]. Similar with Ni- and Cu-based OCs, the use of TiO_2 as supported materials was investigated by Mattisson et al. [38], and they found that Fe_2O_3/TiO_2 show high reactivity but the available oxygen become