Chemical Engineering Journal 309 (2017) 617–627

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Improved reversible redox cycles on MTiOx (M = Fe, Co, Ni, and Cu) particles afforded by rapid and stable oxygen carrier capacity for use in chemical looping combustion of methane

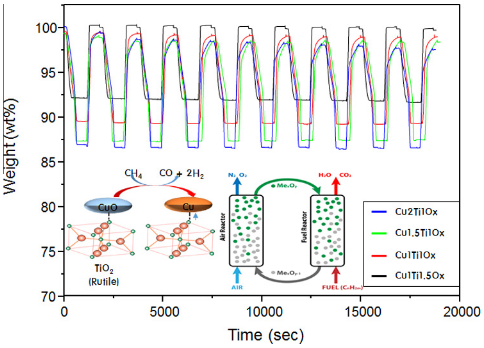
Byeong Sub Kwak[a], No-Kuk Park[b], Si Ok Ryu[b], Jeom-In Baek[c,*], Ho-Jung Ryu[d], Misook Kang[a,*]

[a] Department of Chemistry, College of Science, Yeungnam University, Gyeongsan, Gyeongbuk 38541, Republic of Korea
[b] School of Chemical Engineering, Yeungnam University, Gyeongsan, Gyeongbuk 38541, Republic of Korea
[c] KEPCO Research Institute, Korea Electric Power Corporation, 105 Munji-ro, Yuseong-gu, Daejeon 34056, Republic of Korea
[d] Korea Institute of Energy Research, 152 Gajeong-ro, Yuseong-gu, Daejeon 34129, Republic of Korea

HIGHLIGHTS

- MTiOxs are synthesized for use in the chemical looping combustion of methane.
- The CH_4-TPD and H_2-TPR analyses showed the highest activity on Cu1.5Ti1Ox.
- The variability was exhibited by the different doping elements and concentrations.
- Cu1.5Ti1Ox in CH_4-CO_2/air redox system improved capturing and releasing oxygen.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 May 2016
Received in revised form 4 October 2016
Accepted 8 October 2016
Available online 13 October 2016

Keywords:
MTiOx
Reversible redox cycles
Oxygen carrier
Chemical looping combustion

ABSTRACT

In this study, rutile TiO_2 particles (MTiOx) incorporating 3d-metals, with their electrons more than half-filled, are synthesized for use in the chemical looping combustion of methane. The specific structures are obtained by doping the M-sites with Fe, Co, Ni, and Cu (FeTiOx, CoTiOx, NiTiOx, and CuTiOx), and they have the same M/Ti molar ratio of 1.0. XRD, SEM, CH_4-TPD, TGA, and BET techniques were used to characterize the prepared materials. The XRD results confirmed that all of the prepared materials possessed pure hexagonal phases in the case of Co1Ti1Ox and Ni1Ti1Ox and mixed formations composed of metal oxides and rutile TiO_2 in the case of Fe1Ti1Ox and Cu1Ti1Ox. The CH_4-TPD and H_2-TPR analyses showed that the highest adsorption is obtained on CuTiOx, in particular on Cu1.5Ti1Ox. The oxygen carrier capacities of the samples were measured in H_2 (FR)/air (AR) and CH_4-CO_2 (FR)/air (AR) redox systems at 850 °C using TGA analysis. Their variability was shown to be associated with the different doping elements and doping concentrations. In particular, the Cu1.5Ti1Ox material in the CH_4-CO_2 (FR)/air (AR) redox system exhibits oxygen uncoupling behaviour, leading to improved capture and release of oxygen compared to the other materials.

1. Introduction

The world now has a better understanding of climatic systems and the long-term impact of rising temperatures of the atmo-

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* Corresponding authors.
E-mail addresses: jibaek@kepco.co.kr (J.-I. Baek), mskang@ynu.ac.kr (M. Kang).

http://dx.doi.org/10.1016/j.cej.2016.10.040
1385-8947/

sphere. In this respect, the anthropogenic emissions of CO_2 are regarded as the most prevalent ones aggravating global warming. These atmospheric emissions are the outcome of the rapidly increasing energy demand, which are mainly satisfied using fossil based fuels. Therefore, investigations into the sequestration of CO_2 and the development of renewable power sources have been on the rise since the beginning of the last decade [1–3]. The available CO_2 capturing processes can be classified into three categories based on their approach: the first is pre-combustion [4,5], the process of producing hydrogen from a hydrocarbon or carbonaceous fuel with the help of steam, the second is oxy-fuel combustion [6,7], which uses pure oxygen obtained from cryogenic nitrogen separation from air (CLC), and the third is post-combustion [8,9], where a CO_2 rich flue gas is subjected to an absorption and/or adsorption process over a suitable solvent or solid sorbent or alternatively to membrane separation. With respect to the technologies involved, chemical looping combustion (CLC) has been identified as the most promising one. CLC is capable of delivering performance and efficiency without compromise, as shown in Scheme 1. The generalized reaction stoichiometry for both the fuel reactor (FR) and air reactor (AR) can be expressed as in [10,11]: a metal known as an oxygen carrier is circulated between these two interconnected reactors, (FR) and (AR). The solid carrier in its oxide form provides the oxygen needed for combustion in the FR. The oxygen depleted solid material is then transferred to the regenerator to be re-oxidized in the AR, and then recycled back to the fuel reactor. Therefore, the separation of the fuel and air reactors avoids the dilution of the flue gas stream with nitrogen, and the flue gas is constituted primarily of carbon dioxide and water vapour.

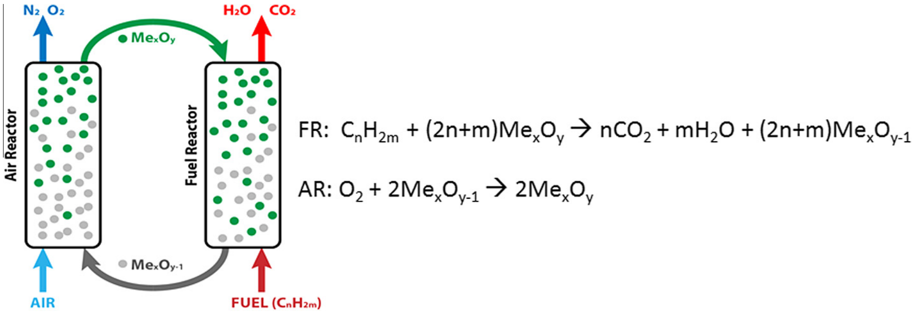
There are transition metal-oxides such as Ni [12], Cu [13], Co [14], Fe [15], and Mn [16] which are regarded as good oxygen carrying candidates. In particular, Ni-based materials are known to have good performances as an oxygen carrier. However, they were not always found to be appropriate in transporting the desired amount of oxygen. This is due to the tendency of the metal oxides to react with the support, forming stable and less reactive solid-solutions. For example, the formation of $NiAl_2O_4$ [17,18], in the case of NiO supported over alumina, reduces the oxygen carrying capacity and causes poor reducibility in CLC. Similar observations were found in the case of MgO support materials due to the formation of the $Mg_{0.4}Ni_{0.6}O$ spinel structure [19]. In addition, the lowering of the reactivity and deactivation as a function of the number of cycles due to low mechanical strength was observed for NiO supported on SiO_2 [20]. Otherwise, the spinel formation ($CuAl_2O_4$) [21] resulted in high reactivity similar to that of NiO-based catalysts. The use of a highly reactive Cu-based oxygen carrier was reported in the literature over a variety of supports such as γ-/α-Al_2O_3 [22,23], bentonite [24], MgO [25], SiO_2 [26], and ZrO_2 [27] using different preparation techniques. As another example, the surface formation of spinel $FeAl_2O_4$ [28] or $FeTiO_3$ [29] was reported to have a beneficial effect on achieving complete fuel conversion to CO_2 and H_2O. However, a drastic drop in reactivity was found when using Fe_2O_3/SiO_2 due to the formation of iron silicates [30].

In spite of the significant progress in CLC technology, its commercialization is still subject to the availability of suitable oxygen carriers. This includes the periodic replacement of oxygen carriers, solid circulation rates between reactors, desired fuel and solid conversion to achieve maximum combustion efficiency, and stability. TiO_2 is widely employed as a key element in solar energy conversion based on dyes [31], photocatalysis [32], electronic circuits [33], and dielectric mirrors [34]. Thus, the present study considers the TiO_2 support, with its larger oxidizing power, easier flow of electrons, and more oxygen vacancies. In particular, oxygen vacancies are prevalent defects in TiO_2 and play a critical role in determining the surface and electronic properties of TiO_2 [35]. In photocatalytic system, it has been reported that the electronic structure, charge transport, and surface properties of TiO_2-based metal oxides are closely related to oxygen vacancies [36]. Theoretical and experimental studies revealed that the excess electrons located on the oxygen vacancies influence surface adsorption and reactivity of key adsorbates such as O_2 or H_2O on TiO_2 [37]. In particular, the oxygen vacancy increase in the metal-loaded or incorporated TiO_2 materials compared pure TiO_2, because of their more structural defects. Thus TiO_2 materials incorporating 3d metals, with their electrons more than half filled, as new oxygen carriers for CLC application are introduced. The reactivity and stability of the prepared $MTiO_X$ oxygen carriers under high thermal stresses, similar to the ones an oxygen carrier may experience in a CLC process, are described. The oxygen carrier reactivity data were obtained using two CLC fuels (H_2-N_2 and CH_4-CO_2) under both fixed bed conditions using a TGA apparatus.

2. Experimental

2.1. Preparations of M (M = Fe, Co, Ni, and Cu) TiOx materials for use as oxygen carrier

MTiOx materials were prepared using a conventional sol–gel process: 0.1 mol of metal (II) chloride ($MCl_2{\cdot}6H_2O$, M = Fe, Co, Ni, and Cu, Junsei Co, Japan) and 0.1 mol of titanium tetraisopropoxide (TTIP, Junsei co., Japan) were added to DI water. 99% NH_4OH was dropped into the mixture to obtain a pH of 9.0 for the next step, and the final solutions were stirred vigorously under air conditions at room temperature. The molar compositions were 1 M:1Ti and the resulting suspensions with the precipitate were centrifuged at 3000 rpm for 5 min. Finally, the precipitates were collected and dried in air at 60 °C, and then heated at 1200 °C for 3 h in order to induce their crystallization. Four kinds of samples were obtained, and they were named as Fe1Ti1Ox, Co1Ti1Ox, Ni1Ti1Ox, and Cu1Ti1Ox, respectively,



Scheme 1. The generalized reaction stoichiometry for both the FR and AR during the chemical looping combustion (CLC).