EXPERIMENTAL INVESTIGATION OF THE EFFECTS OF FLUIDIZING GAS ON COPPER-MANGANESE MIXED OXIDE'S REACTIVITY FOR CHEMICAL LOOPING COMBUSTION OF CH_4

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Abstract

Cu-Mn mixed oxide is a promising oxygen carrier (OC) for both chemical looping combustion (CLC) and chemical looping with oxygen uncoupling (CLOU). The purpose of this study is to investigate how CO_2 as the fluidizing agent affects its reactivity with CH_4. Cu34Mn66 was synthesized with 34wt.% CuO and 66wt.% Mn_3O_4 and tested in a batch fluidized bed reactor. Length of the reducing period for Cu34Mn66 was found to be an important parameter while determining the effect of CO_2. For short reducing period, which occurs in CLOU, no significant change as a result of CO_2 fluidization was observed. However, for longer reduction periods (characteristic of CLC), the Cu and MnO reduced phases catalyze CH_4 dry reforming and reverse water gas shift reactions (RWGS). The extent of the RWGS reaction depends on the feed CO_2/CH_4 ratio. For $CO_2/CH_4>1$ in the feed, the RWGS is more likely to occur resulting in $CO/H_2>1$ in the product stream. When $CO_2/CH_4<1$ in the feed, the ratio of CO/H_2 becomes roughly equal to 1, which could be a result of dry reforming of CH_4. The influence of CO_2 resulting in CO and H_2 formation should be avoided to achieve complete CH_4 combustion to CO_2 by adjusting the residence time of the OC particles in the fuel reactor.

Keywords

CO_2 capture, Cu-Mn mixed oxide, Chemical looping combustion.

Introduction

Chemical looping combustion (CLC) is a CO_2 capture technology where the fuel is oxidized by a metal oxide, called the oxygen carrier (OC), in the fuel reactor that avoids direct contact between the fuel and air.

$C_nH_m+(2n+½m)MeO \rightarrow nCO_2+ ½mH_2O+(2n+½m)Me$ (1)

The reduced OC is regenerated by air oxidation in the air reactor and recycled back to the fuel reactor.

$Me+ ½ O_2 \rightarrow MeO$ (2)

A variant of CLC is chemical looping with oxygen uncoupling (CLOU) where the OC releases O_2 at high temperature and the released O_2 oxidizes the fuel.

$Me_xO_y \leftrightarrow Me_xO_{y-2} +O_2$ (3)

In CLOU, both released molecular O_2 and lattice oxygen are available for combustion. CLC/CLOU processes are usually operated in two interconnected fluidized bed reactors with OC particles continuously circulating between them. For solid fuel combustion, CO_2 and steam are used for fluidization and gasification (Lyngfelt et al., 2001; Mattisson et al., 2009). If gasification is not required (CLOU), CO_2 is preferred (Gayán et al., 2012). The reduction behavior of OCs with fuel is affected by the fluidizing gas (Cuadrat et al., 2012; Merrette and Whitty, 2018) even though the oxygen uncoupling ability is not (Gayán et al., 2012). However, very few studies (Langørgen et al., 2017) have investigated the effects of CO_2 fluidization on CH_4 conversion. Therefore, the purpose of this study is to investigate how Cu34Mn66's reactivity with CH_4 is affected by CO_2 fluidization.

Results

Cu34Mn66 was synthesized by 34wt.% CuO and 66wt.% Mn_3O_4 and was tested in $9\%CH_4 + 5\%N_2$ + balance CO_2 (Figure 1) and $9\%CH_4$ + balance N_2 (Figure 2) at 900^0C.

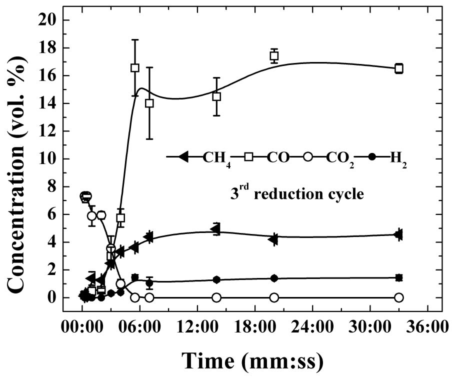

Figure 1: CH_4 oxidation profile in CO_2 fluidizing gas

When the reduction period is short (CLOU), CH_4 oxidation profile is similar for both CO_2 and N_2-rich atmospheres. However, during CO_2 fluidization, for longer reducing time, a significant amount of CO and small amount of H_2 are observed. On the other hand, in N_2-rich atmosphere, at around 7 min. nearly all the fed CH_4 remains unreacted and very small amount of CO and H_2 are produced. This indicates that most of the oxygen is depleted at 7 min. and the OC is reduced to Cu and MnO. Therefore, there should not be enough O_2 to participate in CH_4 conversion for 33 min.

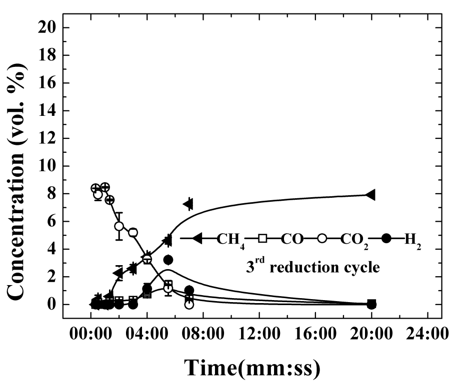

Figure 2: CH_4 oxidation profile in N_2 fluidizing gas

To investigate the reason behind CO and H_2 production, several gas mixtures with 9%CH_4 + X%CO_2 + balance N_2, where X = 2.5, 9, 18, 36 and 91, were fed over oxygen carriers reduced with CH_4-N_2 for 7min. (Figure 3). With the gas mixture of 91% CO_2 ($CO_2/CH_4>1$), nearly the same amount of CO and H_2 are produced as observed in Figure 1. This indicates that the CO_2 used for fluidizing the particles reacts with CH_4 and produces CO and H_2. CO and H_2 could form as a result of CH_4 dry reforming reaction. However, for dry reforming of CH_4, the produced H_2/CO is 1, which is not observed here. Instead, the H_2 amount is much lower than the CO. It can be speculated that in CO_2-rich atmosphere, along with the reforming reaction, reverse water gas shift reaction (RWGS) reaction also occurs. When $CO_2/CH_4<1$, H_2/CO of the product stream is around 1, which is the ratio expected from the dry reforming reaction. It is likely that CO_2 is the limiting reactant at low concentration and cannot take part in the RWGS reaction. When the CO_2 amount in the feed increases, H_2 concentration decreases as a result of the RWGS reaction. It can be concluded that the reduced oxygen carrier can catalyze both CH_4 dry reforming and RWGS reactions.

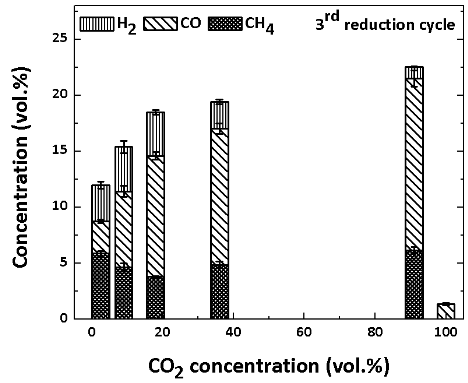

Figure 3: CO_2 effect on CO and H_2 formation

Conclusion

For short reducing period (CLOU), CO_2 fluidization does not affect CH_4 oxidation. However, when Cu34Mn66 is fully reduced to Cu and MnO, both CH_4 dry reforming and RWGS reactions occur due to catalytic activity of the reduced phases either via singular or synergetic catalytic effects between them. The residence time of the particles in the fuel reactor could be adjusted to prevent the undesired CO and H_2 formation.

Acknowledgement

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