Syngas Chemical Looping Combustion using a Fluidizable Ni-Co-La/γ-Al_2O_3 Oxygen Carrier

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Highlights

- A stable and highly performing oxygen carrier 20Ni1Co5La/γ-Al_2O_3 was developed.
- The implemented preparation method secures an oxygen carrier with enhanced reactivity.
- This oxygen carrier is suitable for syngas conversion resulting from biomass gasification.
- The oxygen carrier is compatible with the desirable 550-650°C in biomass catalytic fluidized beds.

1. Introduction

Biomass steam gasification produces a blend of H_2, CO, CH_4 and CO_2, designated as syngas. Syngas can be further combusted using fluidizable oxygen carriers (OC). This operation is known as Chemical Looping Combustion (CLC). With this end, a Ni-based oxygen carrier is implemented with a Co and La modified γ-Al_2O_3 support. This type of OC limits $NiAl_2O_4$ formation. The evaluation of this highly performing OC was developed using the fluidized CREC Riser Simulator reactor at 550-650°C, 5-40s and with a 1-2 oxygen carrier/fuel ratio. It is shown that 60-92% CO_2 yields can be obtained within these operating conditions.

2. Materials and Methods

Oxygen Carrier (OC-Ref) and Syngas as Fuel

This novel nickel on γ-alumina OC was prepared using an Incipient Wetness Impregnation (IWI) method as described in previous research[1]. This OC also includes Co and La additives. Co and La additives have valuable effects on both $NiAl_2O_4$ and carbon formation reduction, respectively [1]. Syngas is a typical biomass gasification product[2]. A syngas was simulated in the experimental runs using a 20v% CO, 10v% CH_4, 20v% CO_2 and 50v% H_2 mixture.

Preparation of a New Fluidizable and Highly Performing Oxygen Carrier (HPOC)

In spite of the valuable progress made with OCs by our research team [2,3], the 750°C calcination temperature used was shown to lead to: a) strongly bounded Ni species on alumina and b) undesirable $NiAl_2O_4$ [1]. These species inherently limit the OC oxygen capacity in the 550-650°C operating range. To circumvent this, a new highly performing OC was prepared by reducing all the formed nickel species at 900°C for 2 hours and this prior to 750°C calcination. This methodology ensures the complete decomposition of strongly bounded Ni on alumina, as well as that of $NiAl_2O_4$. This yields a re-dispersing nickel phase which has little interaction with the γ-alumina support. This new HPOC can provide more than 90% of the nominal oxygen lattice at temperatures between 550-650°C. The promising HPOC was characterized using BET, XRF, XRD, H_2-TPR, NH_3-TPD and pulse chemisorption.

CREC Riser Simulator and Product Analysis

CLC runs of syngas and the new OC were performed using the CREC Riser Simulator. This is a mini-fluidized bed reactor that operates under batch conditions and is particularly designed for oxygen carrier evaluation at expected industrial process conditions. An automatic valve allows the transfer of products to an online gas chromatograph (GC) to detect all product chemical species (CO, CH_4, CO_2 and H_2) accurately.

3. Results and Discussion

Figure 1 reports an H_2-TPR (Temperature Programed Reduction) of OC analysis showing that the new HPOC is very active, yielding more than 90% of the anticipated lattice oxygen in the 400-600°C range. One should notice that the reference OC (OC-Ref) yielded 45% of the available lattice oxygen at that temperature range. Figure 2 compares the XRD patterns of the new HPOC and the reference OC. One can observe that smaller and sharper nickel aluminate peaks were observed for the HPOC at 37.01 and 45.1 degrees in the 2θ scale.

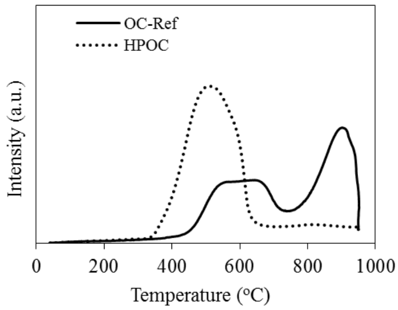

Figure 1. H_2-TPR Profiles of HPOC and OC-Ref. Operating conditions: 10%H_2-Ar, 50 ml/min., temperature ramp of 15°C/min up to 950°C with 10 min. holding time.

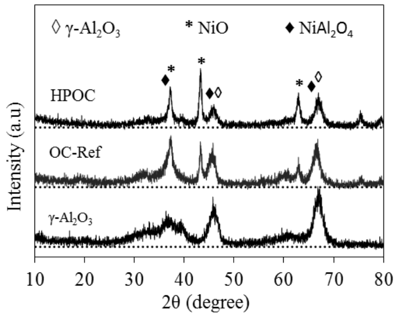

Figure 2. XRD Patterns for HPOC and OC-Ref. The dotted line represents signal baseline.

Table 1. OC-Ref and HPOC Characterizations		
	OC-Ref	**HPOC**
BET Surface Area, m^2/g	107.5	95.2
Pore Volume, cm^3/g	0.37	0.35
Avg. Pore Diameter, A	137.7	146.8
H_2 Uptake, cm^3/g (STP)	54	50
NH_3 Uptake, cm^3/g (STP)	5.2	4.1
Ni Dispersion%	0.85	1.27
Crystal Size(nm) , d_v	115	77

Table 1 reports the oxygen carrier characterizations in terms of BET, pore volume and average pore diameter. One can notice that the HPOC displays structural properties in a close range with respect to the OC-Ref. Table 1 also shows that the HPOC involves higher metal dispersion with smaller Ni crystallites, with all this pointing to its higher reactivity.

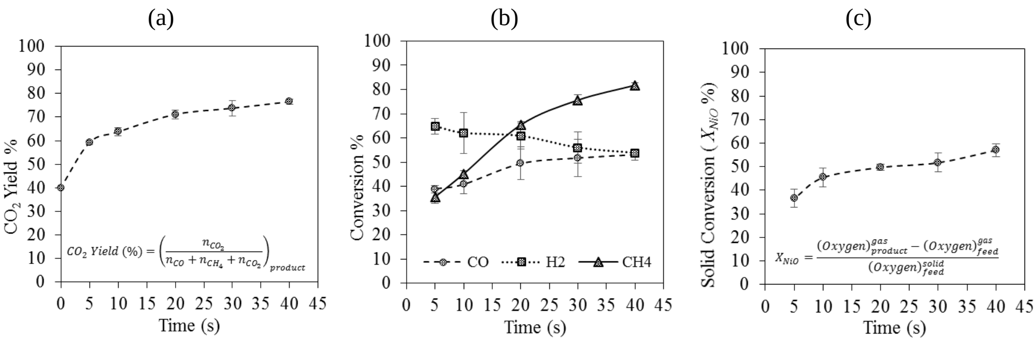

Figure 3: Syngas Conversion at 600°C Using the HPOC for ψ=1 (stoichiometric values): (a) CO_2 yield, (b) Syngas component conversion for CO, H_2 and CH_4 (c) HPOC conversion. (Every reported data point represents the average for more than 3 runs).

Table 2: Effect of Stoichiometric Values (ψ) on Syngas Conversion (at 600°C and 30s reaction time)

		ψ=1	ψ=0.5
CO_2 Yield		73.8	87.2
Conversion %	CO	51.8	78.8
	H_2	55.9	87.8
	CH_4	75.6	79.6
Carbon wt%		~ 0.07	

Note: ψ= ratio of oxygen to be consumed over maximum available oxygen.

Figure 3 reports the CO_2 yields and the CH_4 conversion steadily increasing with reaction time for ψ=1. It is also shown that CO and H_2 conversions stabilize and decrease respectively for ψ =1. These trends were attributed to the influence of reforming reactions under OC starving oxygen conditions. Table 2 also shows that adjusting the OC oxygen supply to ψ=0.5, it leads to all CO, H_2 and CH_4 species being 78-88% converted.

4. Conclusions

A new fluidizable oxygen carrier (HPOC) is prepared and experimentally studied at 600°C for the conversion of synthesis gas. Its high performance is demonstrated using lower than maximum oxygen consumption (ψ=0.5) with methane dry reforming and coke formation being prevented.

References

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Keywords
Syngas; CLC; Oxygen Carrier; Nickel Aluminate