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Improved Oxygen Carriers for Cleaner Energy Generation through Chemical Looping Combustion

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Chemical looping combustion (CLC) is one of the most promising technologies to get sequestration ready CO₂ stream, with high overall efficiency and lower energy penalty. The success of the CLC system is dependent greatly on finding suitable oxygen carriers, efficient reactors, coal gasification and many other aspects. Ceria promoted LaMnO₃ was evaluated with steady state fixed bed reactor for methane combustion and characterized using XRD, SEM initially and after four reduction-oxidation cycles. Results of multi cycle reduction-oxidation tests showed that the reactivity of oxygen carrier remained high and quite stable after four reduction-oxidation cycles.

1. Introduction

CO₂ is the major anthropogenic greenhouse gas (GHG) emitted into the atmosphere, leading to disastrous impacts on environment. The main contributors to the CO₂ emissions are power generation from fossil fuels, industrial activities and transport sector. CO₂ emissions have been correlated to increase in global average air and ocean temperatures, widespread melting of snow and ice and rising sea level, climate change, in addition to many other indirect GHG effects^{1,2}. Carbon based fuels for energy generation have been identified as the major source of GHG emissions, while their continuous use is also predicted in absence of any other suitable alternative. It is therefore necessary to explore the possibilities of CO₂ sequestration as a short and medium term environmental options.

The emission reduction of the largest GHG contributor i.e. CO₂ can be achieved by three means. First option is improving the energy efficiency, thereby emitting lesser CO₂ per unit of fuel consumed. This is a preventive and certainly a lucrative option in terms of fuel savings, however, has practical limitations (thermodynamic cycle efficiency limit). The second option is use of alternative clean fuels (hydrogen, solar, bio diesel etc.) and lower GHG intensive fuels like natural gas. The third option considered is 'Carbon Capture and Sequestration' (CCS) or "CO₂ Capture and Storage". This is obviously a post combustion treatment option and would be essentially required, considering the present and projected use of carbon based fuels. The purpose of the CO₂ separation and capture is to isolate or pre-concentrate CO₂ from its high volume sources in a form suitable for its transport and subsequent sequestration or long term storage. Efficient CO₂ capture from combustion systems is critical for the CO₂ sequestration as it substantially reduces cost as well as overall energy penalty. Extensive R&D efforts are therefore, underway to develop new approaches to

capture and store or sequester the CO₂ to avoid its release into the atmosphere.

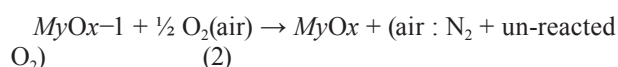
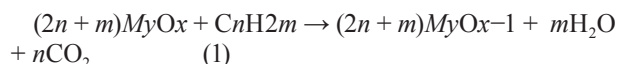
In order to capture CO₂, there are currently a number of available processes as follows:

- (i) Pre-combustion, in which the fuel is de-carbonized prior to its combustion,
- (ii) Oxy-fuel combustion, which normally referred to use of pure oxygen obtained from cryogenic or other separation options from air (CLC in a way is an option under this category) and
- (iii) Post-combustion separation, which separate CO₂ from the flue gases using different approaches.

Most of the techniques explored so far are energy intensive, resulting in a significant decrease of the overall combustion efficiency and consequently result in a overall cost increase in the electricity produced. Chemical Looping Combustion (CLC) presents a potential option to avoid the CO₂ capture step and likely to have a lower overall energy penalty. Chemical looping combustion is the process in which, metal oxides (or other suitable material), rather than air or pure oxygen, provide the oxygen required for combustion. The distinct advantages of CLC are- avoidance of CO₂ separation step, prevention of NO_x emissions and improved overall efficiency. Nearly pure CO₂ is obtained in the exit gas stream following condensation of H₂O, ready for subsequent sequestration without costly purification /pre-concentration. Considering all these factors, chemical-looping combustion appears to have the potential for delivering a most efficient and low cost option for cleaner carbon based energy. This process was initially proposed to increase thermal efficiency in power generation stations, but later on identified as having inherent advantages for CO₂ separation with minimum energy penalty.

CLC process consists of two interconnected, conventionally fluidized bed reactors, an air reactor and

a fuel reactor. CLC uses solid oxygen carrier to transfer oxygen from air to fuel reactor. In fuel reactor, fuel is oxidized by oxygen of the oxygen carrier. The exit stream of fuel reactor has two components, CO₂ and H₂O. The pure form of CO₂ can be readily extracted from fuel reactor by condensing water vapors. After completion of fuel oxidation, reduced metal oxide is transported to air reactor, where it is regenerated or reoxidized¹⁻³). The overall process can be represented through the following chemical equations:



Where, MyOx represents metal oxide oxygen carrier.

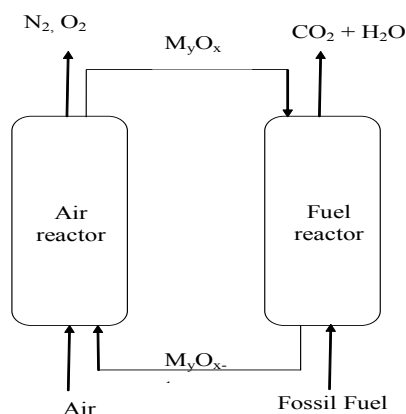


Fig. 1 Schematic representation of chemical looping combustion system.

The oxygen carriers reported for CLC are usually transition metal based such as Ni, Cu, Fe, Co, and Mn due to their favourable reductive/oxidative thermodynamics. Various support materials, namely Al₂O₃, MgAl₂O₄, ZrO₂, and TiO₂^{1,4,5} are used to enhance some of the desirable characteristics of oxygen carrier particles. Ni-based oxygen carriers are considered among the most suitable for the above application, but for improved mechanical strength of oxygen carriers, NiO⁶) is generally supported on YSZ, Al₂O₃, NiAl₂O₄, SiO₂, bentonite, and as NiO/hexa aluminate^{7,8}), whereas NiAl₂O₄ is one of the best supports reported so far. Some of the perovskites are also reported for CLC application^{1,2}). The present research work is based on the modified perovskite type oxygen carriers for their possible applications in CLC. Perovskites with general structural formula ABO₃, have been suggested as substitutes for noble metals in electrocatalysis and in the complete oxidation of carbon monoxide, methane, hydrocarbons and chlorinated hydrocarbons. The ideal structure of the perovskite type oxide is cubic. A and B are usually rare earth and transition metal cations, respectively, for which the corresponding perovskites

show a high activity and thermal stability. B cations have octahedral coordination with oxygen and A cations are located in the dodecahedral lattice position. Although, theoretically perovskites can not be considered as high oxygen carrying materials, their multi-cycle redox operation including that reversibility of structure, thermal stability as well as catalytic activity could be some of the useful properties to make them potential candidates as oxygen carrier (OC) or CLC material.

In the present study, ceria promoted LaMnO₃ was explored as an oxygen carrier. Methane was used as a combustion fuel. The substituted and promoted LaMnO₃ on the catalytic properties for complete oxidation of hydrocarbons has been extensively studied earlier. The oxygen carrier was subjected to four successive cycles of combustion. Fresh and used oxygen carriers were characterized by XRD and SEM.

2. Experimental

2.1 Preparation of oxygen carrier

CeO₂ promoted LaMnO₃ type perovskite (La_{1-x}Ce_xMnO₃ + CeO₂) was synthesized using co-precipitation method by using ammonium hydroxide as precipitating agent. Lanthanum nitrate, cerium nitrate and manganese nitrate were taken in 0.6:0.4:1 molar ratio with respect to metal content and dissolved in requisite quantity of distilled water, followed by precipitation in NH₄OH solution. The precipitate is filtered, washed and then dried at 110 °C. The material so obtained is homogenized and then calcined at 950 °C for 8 h.

2.2 Characterization of carrier

X-ray diffraction patterns were recorded using Rigaku Miniflex II Instrument with Cu Kα1 radiation at 30kV and 15 mA with monochromator. The samples were scanned in 2θ range 10-80° with scanning speed of 3 °C/min. Diffraction peaks were compared with standard database reported in the Joint Committee on Powder Diffraction Standards (JCPDS) cards. The morphological details of the material were studied by scanning electron microscopy (SEM).

2.3 Evaluation of oxygen carrier for methane combustion

Steady state, fixed-bed catalyst evaluation assembly was used to determine oxygen carrying capacity of oxygen carriers. The reactor made of Enkonel alloy was equipped with thermocouple in contact with oxygen carrier bed at atmospheric pressure. 5 g of oxygen carrier was supported by a layer of ceramic wool, and the temperature was maintained with the aid of a PID temperature controlled furnace. The experimental set up consisted of mass flow controllers (Alborg, USA) and a mixing chamber for producing the desired gas mixture. The methane combustion was carried out at 750 °C in the fuel reactor with the simulated gas mixture of 5600 ppm methane, balance by helium having approximate flow rate of 10 ml/min. The low concentration of methane

was used only to get reliable breakthrough time to avoid possibility of measurement error. The effluent stream was continuously analyzed by using a Shimadzu gas chromatograph equipped with a thermal conductivity detector (TCD). Oxygen carriers were pre-treated for 1 hour in helium flow at 300 °C, prior to evaluation, to remove any volatile contaminant and adsorbed gases. Oxygen carriers were re-oxidized in 20 % oxygen for 30 min at 800 °C, and again flushed with helium flow to remove trace of oxygen present. The same process was repeated again with same conditions for the four successive reduction-oxidation cycles to determine the redox properties and stability of oxygen carriers.

3. Results and discussions

3.1 Characterization of oxygen carrier

Fig 2 presents X-ray diffraction pattern for oxygen carrier, which shows crystalline LaMnO_3 orthorhombic phase and cubic CeO_2 impurity phase as identified through JCPDS database. This also suggests that only a part of the Ceria could be incorporated in perovskite structure, while the remaining is present as a separate phase. X-ray diffraction pattern of oxygen carriers after four reduction-oxidation cycles do not show any difference, except the increase in peak intensity, suggesting increase in crystallinity due to the repeated exposure of oxygen carrier to higher temperature, as well as localized high temperature generated during the combustion reaction. Therefore, XRD confirms the structural stability of oxygen carrier at least for four cycles.

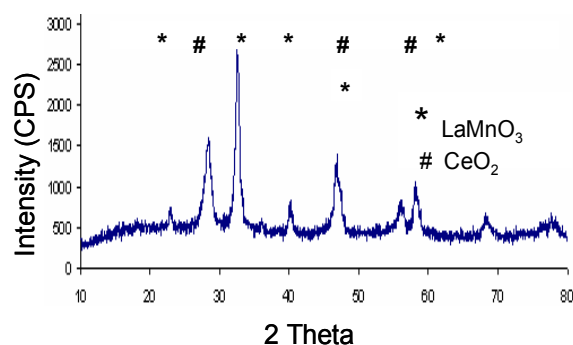


Fig. 2 X- Ray diffraction pattern of oxygen carrier.

The scanning electron microscope (SEM) images of fresh and used sample for four reduction-oxidation cycles at 750 °C are shown in Fig 3. When the two images are compared, we observed small and not significant differences in structural morphology. The images of the fresh oxygen carrier samples have dense surfaces and the grains are irregular, the local environment after reaction shows some sintering of material. However, it is quite interesting to observe practically unchanged methane oxidation capacity despite these morphological changes.

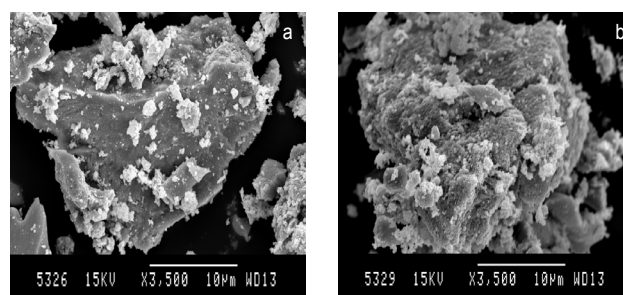


Fig. 3 SEM images of oxygen carriers a) fresh sample b) after four cycles.

3.2 Oxygen carrier evaluation for methane combustion

Fig 4 represents methane conversion by perovskite type oxygen carrier on a time scale at 750 °C. Results clearly show that the methane combustion decreases with time and achieves almost zero conversion after about 10 minutes of reaction in first oxidation cycle. Absence of CO and H_2 confirm that all the reacted CH_4 is converted to CO_2 and H_2O in the first cycle, whereas the subsequent cycles show that methane conversion sustain for little longer followed by a second hump extending quite long. We observed substantial generation of CO through partial oxidation of CH_4 , during this extended period. This could be due to the voids and pores formation by reduction- oxidation cycles with the removal of surface oxygen. This generally favors the exclusion of lattice oxygen, which consequently facilitates the formation of CO and H_2 instead of CO_2 and H_2O . The average amount of methane consumed per gram of oxygen carrier is 0.32 ml. We are further investigating the detailed product analysis with mass balance to study the extent of combustion reaction.

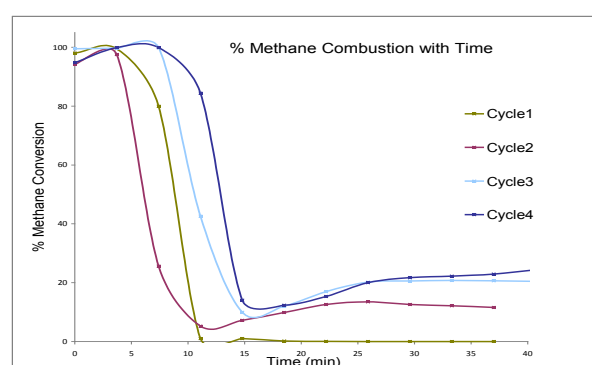


Fig. 4 Methane conversion as a function of reaction time (breakthrough curve) for different cycles (Conditions: CH_4 =5600 ppm `balance He, Flow rate =10 ml/min).

4. Conclusion

Chemical-looping combustion (CLC) offers efficient CO₂ capture from combustion systems, without the need of tedious and energy intensive CO₂ separation step. However, development of new and improved oxygen carriers will be important for the techno-economic feasibility of CLC process. Perovskites offer potential option as oxygen carriers, with their inherent oxygen carrying capacity as well as catalytic properties. The present ceria promoted LaMnO₃ sample displays considerably good and stable behavior over four reduction/re-oxidation cycles. XRD results of used sample confirm the chemical and structural stability of oxygen carrier up to four cycles. The mechanical properties of material need to be examined for its practical utility in fluidized bed reactor. It will be important to analyze this material for more cycles with detailed product analysis. Promotional effect of other elements on the corresponding perovskite and their stability for multiple cycles should also be explored.

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