Co-Ni/Al_2O_3 oxygen carrier for chemical-looping combustion: Reactivity, stability and kinetics study

*Mohammad. M. Hossain, Hugo. I. de Lasa**
Chemical Reaction Engineering Center, The University of Western Ontario, London, ON, Canada N6A 5B9.
*hdelasa@eng.uwo.ca; mhossai4@uwo.ca

Introduction

It is generally accepted that the emission of CO_2 gas is primarily responsible for global warming, which leads the world community to investigate alternative technologies in order to reduce CO_2 drastically. The available CO_2 capture technologies are energy intensive and costly. As a result, important research is currently being developed to improve efficiencies and to reduce CO_2 sequestration cost. Chemical-looping combustion (CLC) is possibly the most promising CO_2 sequestration technologies. CLC involves two interconnected fluidized beds, a fuel reactor and an air reactor, with a solid oxygen carrier re-circulated between the two units. In the fuel reactor, the gaseous fuel is combusted using the structural oxygen of the metal oxide. The reduced oxygen carrier is then transported to the air reactor to be re-oxidized. Completed this operation, the oxygen carrier is re-circulated back to the fuel reactor. In CLC, complete combustion of fuel produces CO_2 and water vapor. Therefore, CO_2 can be recovered easily by condensing the water vapor, without involving an extra step of energy intensive CO_2 separation. Finally, the free-of-water CO_2 can be sequestrated or/and used for other applications. Regarding the outlet gas stream of the air reactor, it contains nitrogen and unreacted oxygen. These gases can be directly release to the atmosphere without environmental impact. In CLC, the formation of NO_x is also negligible because the fuel burns in absence of nitrogen without flame. The large-scale application of CLC is contingent to the availability of suitable oxygen carriers. A successful oxygen carrier material should have high tendency to react with fuel and air, sufficient durability in repeated oxidation and reduction cycles and should not agglomerate in fluidized bed reactors [1]. This study deals with the development of a bimetallic Co-Ni/Al_2O_3 oxygen carrier suitable for a fluidized bed CLC process.

Experimental and Methods

The bimetallic oxygen carriers were prepared via an incipient wetness technique (Ni/Co = 40). The reactivity and stability of the prepared oxygen carrier particles under repeated reduction/oxidation was established in CREC fluidized riser simulator [2] using CH_4 and air for the respective cycles. The reduction cycle was carried out at 680ºC and the oxidation was conducted at 525ºC.

A solid-state kinetics for both reduction and oxidation cycles is established using a clarified Avrami-Erofeev model at non-isothermal conditions (Eq. 1) [3].

$$\frac{d\alpha(t)}{dt} = nk_0 \exp\left[\frac{-E_a}{R}\left(\frac{1}{T}-\frac{1}{T_m}\right)\right](1-\alpha)[-\ln(1-\alpha)]^{\frac{(n-1)}{n}} \qquad (1)$$

A least square fitting of the k_0, E_a and n parameters of Eq (1) was implemented using MATLAB and experimental data of this study. Parameters were estimated in 0 to 0.95 conversion range.

Results and Discussion

Analysis of the gases from the CREC Riser Simulator showed both CO_2 and H_2O. The product analysis also showed trace amounts of H_2; with no CO being detected in the combustion product gas sample. The presence of trace amounts of H_2 in the product gas indicates the occurrence of some methane decomposition and reforming. Reactive characterization under multiple reduction/oxidation cycles demonstrates that the Co-Ni/Al_2O_3 particles display excellent reactivity and stability (Fig. 1). The addition of Co in Co-Ni/Al_2O_3 reduced the metal (Ni)–support (Al_2O_3) interactions to facilitate the formation of $CoNiO_2$ and NiO phases and minimize the formation of $NiAl_2O_3$ [4]. Both the $CoNiO_2$ and NiO are easily reducible under studied reaction condition, which helps the bimetallic oxygen carrier to ready react with gaseous fuel (CH_4). The presence of Co also inhibits metal particle agglomeration by maintaining consistent metal dispersion during the cyclic reduction/oxidation process. As a result of that the reactivity of the Co-Ni/Al_2O_3 oxygen carrier remaine stable over the repeated reduction/oxidation cycles. XRD analysis of a fresh sample and a regenerated sample after 10 CLC cycles show that the crystalline phase of the bimetallic oxygen carrier remains unchanged over the reduction/oxidation cycles. It further confirms that the formation of solid solution of Co and Ni ($NiCoO_2$) provides favorable chemical and physical properties producing improved performance in a cyclic reaction. The Avrami-Erofeev model with random nucleation mechanism (for n = 1) is found to describe the experimental data adequately, with various parameters being determined with their appropriate statistical spans for good fitting. The estimated activation energies are found to be 45 kJ/mole and 44 kJ/mole for reduction and oxidation Co-Ni/Al_2O_3 receptively, with these consistent with the literature values.

Significance

Highly active and stable Co-Ni/Al_2O_3 oxygen carrier and established solid reduction/oxidation kinetics possibly contribute towards successful large-scale industrial application of CLC processes.

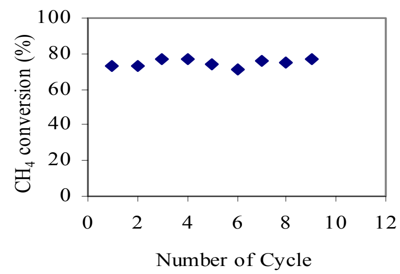

Fig. 1: CH_4 conversion (10 ml CH_4/gm carrier)

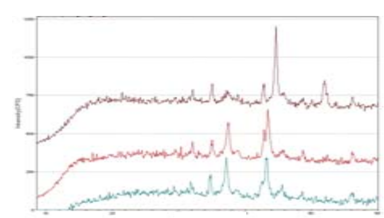

Fig. 2: XRD patterns

References:

[1] Lyngfelt, A., Leckner, B., Mattisson, T., Chem. Eng. Sci., 56, 3101 (2001).
[2] de Lasa, H.I, Riser Simulator, US Patent 5, 102, 628 (1992).
[3] Hossain, M.M.., de Lasa , H.I., submitted, AIChE J. (Dec., 2006).
[4] Hossain M.M., Sedor, K.E., de Lasa, H.I., Chem. Eng. Sci., (accepted, Dec., 2006).