Reactivity assessment and kinetic measurements of methane-fueled chemical looping combustion using supported mixed metals (Ni-Co, Ni-Cu, Ni-Fe) and Al$_2$O$_3$, CeO$_2$, TiO$_2$, and ZrO$_2$ supports as oxygen carriers

Mansour Mohammedramadan Tijani$^1$ Aqsha Aqsha$^2$ & Nader Mahinpey$^1$

$^1$ Department of Chemical and Petroleum Engineering, Schulich School of Engineering, University of Calgary, Calgary, AB, T2N 1N4, Canada.

$^2$ Department of Chemical Engineering, Faculty of Engineering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak Darul Ridzuan, Malaysia.
Abstract:

Introduction

Global warming caused by greenhouse gases (GHGs) emissions has, in recent years, become a great concern internationally. Latest changes in weather patterns can be attributed as one of the possible results of global warming. Greenhouse gases, including carbon dioxide (CO₂), methane (CH₄), water vapour (H₂O), ozone (O₃), nitrogen oxides (NOx) and fluorinated gases (F-gases), are directly tied to global warming because of their increasing concentrations in the atmosphere. The emission portion of carbon dioxide (CO₂) is one of the highest (~64.3%) among the GHGs. The Canadian oil sands resources require additional extraction processes that produce three times more GHG (CO₂) emissions than conventional oil wells. Currently, 61 million tons of GHG emissions per year are produced by the oil sands industry, and this is projected to increase to 104 million tons of GHG per year in 2020. These statistics show the urgency of GHG-reduction technologies for oil sands recovery operations, especially in Alberta where 79.2% of total Canadian oil sands operations are located. Accordingly, carbon capture is a key technology for oil sands operations in Alberta in decreasing GHG emissions. The Chemical Looping Combustion (CLC) process is an alternative process to capture CO₂, which produces a concentrated stream of CO₂ due to the combustion of fuel with oxygen. The combustion of fuel happens in a pure oxygen environment; thus, the formation of nitric oxide and nitrogen dioxide gases is avoided as those gases make the separation of CO₂ expensive and difficult. At complete combustion, water and CO₂ are produced, which can be separated by condensation. The produced CO₂ is then compressed and transported to either storage or utilization.

Motivation

Despite many published studies on CLC processes, the commercialization of this technology has been limited due to vital challenges such as the capital costs, inconclusive scientific testing and role of the oxygen carriers. Novel oxygen carriers that have less interaction between the active-sites and supports could increase the selectivity of CO₂ during the combustion of methane, which in turn could reduce solid inventories needed in the reactor system, cost and environmental impact. Less solid inventories in the reactor system could lead to reduction in capital cost and efficiency increase compared to the existing efficiency of 40%-50%. Therefore, the incipient wetness impregnation technique was used to manufacture supported monometallic and bimetallic oxygen carriers using Ni, Co, Cu, Fe and their combination as active-sites deposited on Al₂O₃, CeO₂, TiO₂ and ZrO₂ supports to find efficient carriers for CLC process when methane is used as a fuel.

Novelty

Although the use of Ni-, Co-, Cu- and Fe-based oxygen carriers in the CLC processes has been reported in the literature, identifying the reaction mechanisms and transition phases of metals during the redox reactions has not been fully investigated. Therefore, this work investigates the reaction mechanisms involved in the redox reactions of these metals, as well as their interaction with different supports to enhance their reactivity (high conversion rate, and low activation energy/mass transfer) during the CLC process. The novelty of this work also includes use of the lowest possible metal loading of 10% on supports to clear up any possible agglomeration of particle on supports when the kinetic evaluation is conducted.

Results

The results of this study show decreases in both BET surface area and pore volume of oxidized and reduced samples in air at 800°C and H₂ at 800°C. The greatest surface area reductions were found in Ni-Fe/CeO₂ (78.80%), Ni-Fe/TiO₂ (42.33%), and Ni-Co/ZrO₂ (39.46%) samples. The deceases in surface area is attributed to sintering of particles. The variation in the redox rates with different sample initial weights (5mg to 20mg) is attributed to the mass transfer effect. As the initial weight of the samples increased, the oxidative gas encountered resistance to diffuse inside the product layer of the oxygen carriers. Thus, as the initial weight of the samples is increased, the oxygen carriers’ reactivity decreased. Furthermore, as the reducing gas concentration increased, the reduction profile of all sample and coke formation on the oxygen-free precursors noticeably increased. Three scenarios for
the reaction mechanisms during the oxidation of supported bimetallic oxygen carriers when the H₂-TPR analysis was performed were predicted and are discussed in detail. The attraction energy between the bimetallic and supports during the synthesis increased and resulted in higher reduction temperatures with hydrogen gas, which later showed mass transfer limitations for most samples during the oxidation reaction. The Ni-Co/Al₂O₃, Ni-Co/CeO₂, and Ni-Co/TiO₂ samples reported increases in the oxygen capacity as temperatures increased from 800°C to 1000°C; however, Ni-Co/ZrO₂ showed a stable oxygen capacity (around 9.7%) as temperatures increased. The highest oxygen capacity for other supported bimetallic precursors was mainly found in the supported samples with CeO₂ and TiO₂ at temperatures higher than 850°C, due to further interaction and reduction of supports. Activation energy for the reduction reaction was evaluated at different solid conversions to determine the possible reaction mechanisms that were dominant during the reduction reaction. All possible redox mechanisms are discussed in detail, with the main conclusion being that interaction between precursors and supports during the reduction reaction could be prevented to increase the reactivity of oxygen carriers only once improvements in the chemical stability during synthesis have been accomplished.

Impact

As a result of the increase in fossil-fuel extraction in the recent years, Canada’s CO₂ emissions have risen to around 750 Mt per year per capita. Emissions from the extraction of fossil fuels will continue to increase as the share produced by unconventional oil and gas resources significantly increases. The development of the chemical looping combustion process, especially for unconventional oil and gas operations, will be of special benefit to Canada and conceivably lead to very significant reductions in GHG emissions. The expected outcomes of this work will benefit Canada’s economy through the sustainable and clean production of energy. Potential users of this work will come from the energy sectors, including oil and gas and power generation companies.
Figure 1. H$_2$-TPR intensity profile (A) and mass transfer limitation (B) for the synthesized bimetallic oxygen carriers.
Figure 2. Graphical representation of the CLC process using mixed-metal oxygen carriers with the predicted precursor-support interactions.