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Study and analyses of a CLC oxygen carrier degradation mechanism in a fixed bed reactor

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HIGHLIGHTS

- Determination of an oxygen carrier degradation mechanism.
- Experimental study in fixed bed reactor.
- Physical characterization of the material evolution.
- Description of the causes of attrition and agglomeration phenomena.

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ABSTRACT

This paper deals with the study, analysis and determination of the oxygen carrier degradation in the Chemical Looping Combustion of methane with $NiO/NiAl_2O_4$ as oxygen carrier. A fixed bed reactor fed alternatively with oxygen (5% in Argon) and a mixture of methane (5%) and steam (from 0.3% to 2% in Argon) has been used with. operating temperature ranging from 700 to 850 °C. Without fluidization, and with only 10 cycles of reduction/oxidation, a high degradation of the material has been observed using X-ray diffraction analysis, SEM observations and BET or PSD characterizations. It is shown that this degradation is caused by the carbon, produced by the methane cracking reaction catalyzed by reduced nickel, and deposited at the surface of the material. The contraction and expansion of the elementary particles composing the grains during the CLC reactions is also a cause of the observed degradations. These phenomena of contraction/expansion cannot be avoided, unless the reduction degree of the material is reduced during the cycles. Therefore, an increase of the operating temperature or of the feeding steam concentrations can lead to a decrease of the material degradation.

1. Introduction

The production of carbon dioxide (CO_2) by human activity is one of the main causes of climate changes. In order to reduce the production of this greenhouse gas, carbon capture and storage processes (CCS) are being developed. The Chemical Looping Combustion (CLC) process is an oxy-combustion carbon capture process which receives a growing interest as an efficient and low-cost combustion technology for selective capture of CO_2 (Adanez et al. [1]). In this process, energy is produced by the combustion of different combustibles (such as liquid fuels [2,3], solid fuels [4–14], biomass [15–17], or methane [18–25] with an oxygen carrier. The produced carbon dioxide is not diluted in other gases (like nitrogen) which ensures its high purity. Thus, no additional separation units are necessary to sequester the carbon dioxide.

A sketch of the Chemical Looping Combustion process is presented in Fig. 1. The oxygen carrier used in this process is a metallic oxide which has the ability to release its oxygen in the combustion reactor. The reduced metal, produced by the fuel combustion, is then re-oxidized with air. This process thus needs two parallel reactors: an air (regeneration of reduced oxygen carrier) and a fuel (combustion of fuel with the oxygen carrier) reactors. The oxygen carrier circulates between the two reactors in order to operate in a continuous way. Fluidized beds are generally used in this process (Adanez et al., [1]) and the solid circulates between the two interconnected reactors. In this paper, the reduction of the oxygen carrier will be referred as the reduction step of the process and the oxidation of the oxygen carrier is thus called the oxidation step of the process.

Unfortunately, the CLC process have shown efficiency losses during operating time whatever the oxygen carrier materials [1,14,26–33]. When starting the process, the reactivity of fresh materials, whatever their composition, fluctuates before stabilizing

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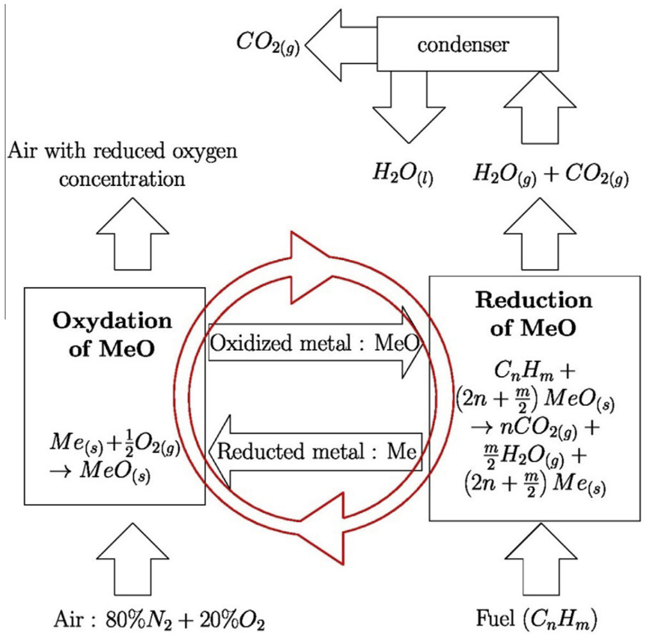

Fig. 1. Chemical Looping Combustion process.

[28–31]. It corresponds to an activation of the material, attributed, according to Medrano et al. to a migration of the active metal species in the material. Thus, after some cycles of reduction/oxidation, the concentration of active metal at the surface of the grains of oxygen carrier increases, which leads to a better and constant reactivity. Blas et al. [26] and Larring et al. [30] have also observed and described these migration phenomena. According to Blas et al. [26], if the material oxidation is performed with only 5% of oxygen, this phenomenon of migration of the active metal in the material can be avoided. Once the material activated, the phenomena of attrition, agglomeration, ageing and deactivation of the oxygen carrier lead inevitably to a decrease of the performances of the process. The main phenomenon responsible for the degradation of the oxygen carrier is supposed to be attrition according to Blas et al. [26]. Indeed, the successive reduction and oxidation of the material, the temperature variation due to reaction and processing, and the circulation of the material in the process induce high constraints which lead to an inevitable attrition of the oxygen carrier. Most of the studies presented in literature attribute this attrition to the solid circulation in the fluidized beds, but in some papers, it may also be the consequences of thermal variations or reaction effects (De Diego et al., [24]). Finally, agglomeration phenomena are also observed in some studies [14,26,28,31]. These phenomena are important in fixed bed reactors, but remain less significant than attrition in fluidized bed reactors. According to Shen et al. [33], a decrease of the material specific surface area during the reactions is also responsible for the oxygen carrier reactivity loss. But much more studies attribute the oxygen carrier morphology variations to the active metal migration [26,30,31]. In some cases a reduction of the material supporting the oxygen carrier has also been observed [26,32,33].

The aim of the work presented in this paper is to study and describe the mechanisms responsible for the degradation of the material. Nickel oxide supported by nickel aluminate (60% NiO/40%$NiAl_2O_4$) was used as oxygen carrier, being a reference in numerous studies (Adanez et al., [1]). The reduction step was performed with diluted methane, and the oxidation was realized with diluted oxygen. In order to estimate the influence of thermal and chemical effects only on the oxygen carrier degradation, a fixed bed reactor was used instead of fluidized beds. Indeed, the fixed bed allows avoiding any friction of the material, and the degradation of the oxygen carrier in this kind of reactor may only be the consequence of chemical and thermal effects. In absence of reaction, the friction between grains can be defined as the main cause of oxygen carrier degradation. The fixed bed reactor was fedalternatively by diluted methane and oxygen to operate the reduction/oxidation cycles. The impact of different operating conditions such as fuel concentration, temperature, water concentration, etc. on the degradation of the material have been studied.

In the next part of this paper, the experimental setup as well as the operating conditions chosen for the fixed bed reactor experiments are detailed. Besides, the different analyses done on the material are presented. Then, an analysis of the experimental results obtained in fixed bed reactor give some information about the different reactions occurring in the reactor. Finally, a mechanism of the oxygen carrier degradation, based on the observed variations of the material morphology, will be developed.

The mechanisms presented in this paper will be used, in subsequent works, to develop a modeling of the fixed bed reactor used in this study. This model should be able to describe the reactivity evolution of the material, based on the kinetic expressions developed in a previous paper (Tilland et al. [34]).

2. Experimental setup and method

2.1. Experimental setup

The aim of the experiments is to determine the various reactions and phenomena occurring in the reactor and also to observe, determine and quantify the degradation mechanism of the material, after several reduction/oxidation cycles. The experimental setup is presented in Fig. 2. It is composed of a fixed bed reactor, equipped with a feeding system and analytical devices.

The reactant (H_2O, CH_4 and O_2) concentrations and flowrates can be adjusted with mass flow controllers and a bubbler. An oven allows operating experiments at temperature ranging from 700 to 850 °C. The reacting volume is composed of a cylindrical chamber of 10 mm diameter. The oxygen carrier (NiO (60%)/ $NiAl_2O_4$ (40%)), in powder form, was deposited on a sintered-glass disc. For most of the experiments, 1.4 g of powder with a mean diameter of 212 μm were used, which led to a height of the powder in the reactor of approximately 2 cm. The oxygen carrier was produced by Marion Technology by coprecipitation.

The fixed bed was fed by a mixture of 1–10% of methane in argon, for the reduction step of the process. The gas feeding the reactor also contained a fraction of water, ranging from 0.5 2%. Mixtures of 1–10% of oxygen in argon, were used for the oxidation step. Continual quantitative data about the composition of the gas phase leaving the reactor were obtained with the coupling of a gas micro-chromatograph and a mass spectrometer. The gas phase living the reactor was analyzed by a Quadstar Mass Spectrometer (Omnistar GSD 320 O1) which gives qualitative information about the gas compositions. A gas micro-chromatograph (Agilent 3000A) was thus used to calibrate the mass spectrometer. This device is composed of two modules consisting of a molecular sieve column (molsieve 5A) using argon as carrier gas and a Poraplot-U column, using helium as a carrier gas. The mass spectrometer signal for water was calibrated with a mass balance on the gaseous species leaving the reactor.

2.2. operating conditions

Operating conditions have been chosen to promote the oxygen carrier degradation in short operating times. Consequently, unlike industrial conditions, the material was totally reduced during each