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Influence of the regeneration conditions on the performances and the microstructure modifications of $NiO/NiAl_2O_4$ for chemical looping combustion

Lucia Blas [a,*], Sophie Dorge [b,1], Laure Michelin [c,2], Patrick Dutournié [c,3], Arnold Lambert [d,4], David Chiche [d,5], Stéphane Bertholin [d,6]

[a] NS3E, ISL-CNRS-UdS (Nanomatériaux pour les Systèmes Sous Sollicitations Extrêmes), UMR 3208, French-German Research Institute of Saint-Louis, 5, rue du Général Cassagnou, B.P. 70034, 68301 St Louis, France
[b] Laboratoire Gestion des Risques et Environnement, Université de Haute Alsace, 3 bis, rue Alfred Werner, 68093 Mulhouse, France
[c] Institut de Science des Matériaux de Mulhouse (IS2M), UMR 7361 CNRS-UHA, 3 bis, rue Alfred Werner, 68093 Mulhouse, France
[d] IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France

HIGHLIGHTS

- Total Reduction Capacity of the OC depends on temperature due to the contribution of $NiAl_2O_4$.
- Oxidation with low oxygen concentration increases oxygen carrier lifetime and CO_2 purity.
- A nickel rich layer is observed at the surface of the particles reoxidized under air.
- OC regeneration under air increases particle aggregation and reduces the specific surface area.

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ABSTRACT

This work aims to study the evolution of $NiO/NiAl_2O_4$ redox performance with CO as fuel for Chemical Looping Combustion (CLC) applications. The oxygen carrier (OC) was investigated under alternating oxidizing and reducing conditions in a fixed bed reactor simulating the cyclic conditions of CLC. The study of the operating temperature influence reveals that total reduction capacity increases with temperature, due to the reaction of the binder $NiAl_2O_4$. Regeneration step performed under low oxygen concentration (5 vol.%) shows that the decrease in total reduction capacity during multiple cycles is minimized and the purity of produced CO_2 is higher. Therefore, carrying out the regeneration step at lower oxygen concentrations can increase oxygen carrier lifetime. Characterization studies revealed the formation of a nickel rich layer at the surface (up to 20 μm thick at 900 °C) and a partial sintering of particles regenerated under 20 vol.% of oxygen. However, these phenomena are not observed on the particles regenerated under low oxygen concentration. The formation of this layer can be explained by the fact that nickel oxidation is carried out by migration of Ni^{2+} cations through the layer of NiO initially oxidized at the surface of the particle, the layer becomes thicker during cycles, because NiO does not return to its initial position. At higher temperature, the diffusion velocity increases and therefore the layer formed is thicker.

Specific surface area of the oxygen carrier decreases as cycles number increases from 9.4 m^2/g for the fresh material to 4.4 and 2.3 m^2/g after thirty cycles at 750 °C and 900 °C respectively. The same trend is observed for porous volume. However, the decrease is lower when particles are regenerated under low oxygen concentration (6 m^2/g).

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* Corresponding author. Tel.: +33 3 89 69 56 72; fax: +33 3 89 69 50 74.
E-mail addresses: lucia.blas@isl.eu (L. Blas), sophie.dorge@uha.fr (S. Dorge), laure.michelin@uha.fr (L. Michelin), patrick.dutournie@uha.fr (P. Dutournié), arnold.lambert@ifpen.fr (A. Lambert), david.chiche@ifpen.fr (D. Chiche), stephane.bertholin@ifpen.fr (S. Bertholin).
[1] Tel.: +33 3 89 33 61 59; fax: +33 3 89 33 61 61.
[2] Tel.: +33 3 89 33 67 30; fax: +33 3 89 33 67.
[3] Tel.: +33 3 89 33 67 52.
[4] Tel.: +33 4 37 70 29 30.
[5] Tel.: +33 4 37 70 22 89.
[6] Tel.: +33 4 37 70 25 21; fax: +33 4 37 70 23 09.

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1. Introduction

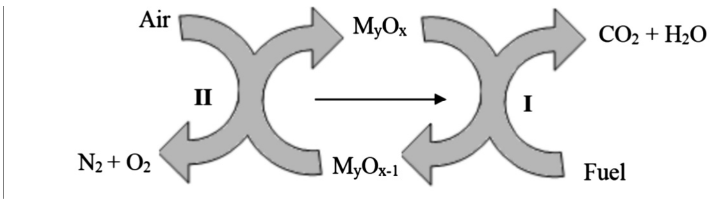
A significant reduction of CO_2 emissions is nowadays required to stabilize the climate at safe levels. Chemical Looping Combustion (CLC) is an innovative technology for energy production with an inherent capture of CO_2. Fig. 1 describes the general scheme of the CLC process. The main characteristic of this technology is that the combustion is performed without contact between the combustible and air. For this, the oxygen is supplied by a solid oxygen carrier (usually a metal oxide M_yO_x) which is prepared with a binder to obtain required mechanical properties. The oxygen carrier is alternatively reduced by the fuel (Eq. (1) in Fig. 1) and reoxidized (regenerated) by air (Eq. (2) in Fig. 1) [1]. The fuel is injected in the combustion reactor where it reacts with the oxygen carrier to produce CO_2 and H_2O. Therefore, after water vapor condensation, almost pure CO_2 is obtained. The oxygen carrier is then reoxidized in the regeneration reactor under air flow. The air flow depleted in oxygen obtained at the regeneration reactor outlet can be directly emitted to the atmosphere. Thus, this technology avoids the separation between CO_2 and nitrogen, which is the most expensive step of CO_2 capture and sequestration [2]. Several investigations have been carried out to enhance the CLC technology performances. The major constraint for large scale application is to find suitable oxygen carriers with sufficient reactivity and stability during successive oxidation/reduction cycles [1]. Ni [3–12], Cu [13–16], Fe [17–22], Mn [23–26] and Co [27,28] oxides are the most promising transition metal oxides for the CLC process. However, various alternative and low cost oxygen carriers have been studied such as mixed oxides [29–31], ilmenite [20,32,33] and $CaSO_4$ [34,35]. The main results showed that the active phase of the oxygen carrier (metal oxide) must be coupled with a binder to avoid metal oxide agglomeration, increase mechanical properties and more broadly prevent process performances degradation [36]. This binder provides a higher surface for reduction reaction and also better mechanical properties to the oxygen carrier [37]. However, the oxygen carrier performances strongly depend on the used binder [6].

Among the studied potential materials for the CLC application, $NiO/NiA_{l2}O_4$ is considered as an efficient oxygen carrier. Indeed, this oxygen carrier exhibits high reactivity with many fuels (CH_4, CO and H_2), good thermal stability (up to 1200 °C) and good mechanical and physical properties [1,38]. Several authors examined the use of γ-Al_2O_3 as a binder for NiO [7,39,40]. They observed that at high temperatures, the Al_2O_3 binder could react with the active phase (NiO) to produce $NiA_{l2}O_4$. Thus, the nickel oxide that has partially reacted with the binder cannot deliver oxygen for the combustion reaction. Consequently, the total reactivity of the oxygen carrier decreases. In order to avoid this problem, Jin et al. [27] proposed the use of $NiA_{l2}O_4$ directly as a binder. Several studies have examined the $NiO/NiA_{l2}O_4$ reactivity using thermogravimetry apparatus [41,42]. The main drawback of this type of analysis is attributed to the diffusional limitations which may occur during reduction reaction. Hence, the obtained results could be hardly extrapolated to large scale plants. Other studies of $NiO/NiA_{l2}O_4$ reactivity were carried out at laboratory scale in fixed bed reactor [43,44], in fluidized bed [10,11] and in pilot plants [12,45]. Authors generally observed good reactivity of $NiO/NiA_{l2}O_4$ to oxidize CH_4, and stability during reduction–oxidation cycles. Ishida et al. [43] observed that after more than 20 cyclic reactions in fixed bed reactor, the particles of $NiO/NiA_{l2}O_4$ looked like fresh ones, showing outstanding regenerability. Studies carried out in fluidized bed reactors showed defluidization tendencies of the material, caused by agglomeration of particles [11]. In a 10 kWth CLC reactor, Johansson et al. [45] showed that chemical and structural changes in particles were minor (no deactivation observed) after 100 h of continuous operation. The same research group [46] obtained a quasi-complete fuel conversion with this oxygen carrier. Kinetic studies for different Ni-based oxygen carriers were also described in literature [47,48].

Nevertheless, the oxygen carrier performance evolution during successive reduction/reoxidation cycles as function of the oxidation phase parameters has not been deeply investigated. Few studies [49,50] have performed the oxidation phase under 5 vol.% of oxygen in order to avoid the high temperature increase attributed to the exothermic oxidation reaction. However, the oxidation parameters effect on the global reduction reactivity was not examined further.

The $NiO/NiA_{l2}O_4$ performance during a long term use has also been examined. Linderholm et al. [46,51] studied the reactivity and the stability of this oxygen carrier (60–40 wt.% $NiO/NiA_{l2}O_4$) in a 10 kWth pilot plant, first, during 160 h and second, during 1000 h using syngas as fuel. They have observed soft particles agglomerates of a few centimeters, which prevent correct particle circulation. Currently, the particle agglomeration mechanism is not well identified. Linderholm et al. [51] suggested that the degree of reduction, size and shape of particles and fuel reactor mixing conditions may have a significant effect on particles agglomeration. Kuusik et al. [52] observed defluidization of the oxygen carrier caused by agglomerates formed through small bridges between the oxygen carrier particles consisting of pure Ni.

Problems related to agglomeration or aggregation observations are often reported in the literature and used to explain reactivity decrease as cycles performed. But, few if any works have investigated agglomeration phenomena in CLC process. According to the literature, three agglomeration phenomena can be observed in these processes [53–57]:



I: Combustion reaction: $$(2n+m)M_yO_x + C_nH_{2m} \rightarrow (2n+m)M_yO_{x-1} + mH_2O + nCO_2$$

II: Regeneration reaction: $$(2n+m)M_yO_{x-1} + \left(n+\tfrac{1}{2}m\right)O_2 \rightarrow (2n+m)M_yO_x$$

Global reaction: $$C_nH_{2m} + \left(n+\tfrac{1}{2}m\right)O_2 \rightarrow mH_2O + nCO_2$$

M_yO_x/M_yO_{x-1}: metallic oxides in oxidized and reduced state

Fig. 1. General scheme of CLC process.