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Thermal stability study of $NiAl_2O_4$ binders for Chemical Looping Combustion application

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HIGHLIGHTS

- The $NiAl_2O_4$ binder of the oxygen carrier ($NiO/NiAl_2O_4$) reacts with fuel.
- $NiAl_2O_4$ progressively decomposes to produce NiO and Al_2O_3.
- The NiO content in the binders increases during CLC cycles.
- The binder reactivity depends on the preparation method (synthesis, temperature).
- Both binders are structurally modified during oxidation–reduction cycles.

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ABSTRACT

The influence of the preparation method of $NiAl_2O_4$ binders on their thermal stability was studied. For this purpose, the reactivity of two different $NiAl_2O_4$ binders with CO as fuel was studied in a fixed bed reactor device. Successive oxidation–reduction cycles were performed on the two binders to study their reactivity with the fuel and their structural modifications as cycles proceed. Results reveal that binders are not inert in reducing atmosphere; they both react with the fuel to produce CO_2. The total reduction capacity (TRC) of the first binder (B1, synthetized by pyrolytic pulverization) increases during the first cycles and levels off after 20 cycles. However, the TRC of the second binder (B2, synthetized by calcination of a mixture of Ni(OH) and γ-Al_2O_3), increases progressively and reaches a maximum after 80 cycles. The growing amount of available oxygen in the binders leads both binders to structural modifications. X-ray Diffraction studies performed on fresh and aged binders presented a shift of the peaks related to $NiAl_2O_4$. Moreover, quantitative X-ray Diffraction studies and Temperature Programmed Reduction measurements were performed in order to quantify the NiO present in each binder before and after oxidation–reduction cycles. These experiments revealed the presence of NiO in fresh binders due to the preparation method, and an increase of this amount after oxidation–reduction cycles. Therefore, $NiAl_2O_4$ in the binder is progressively decomposed producing NiO and Al_2O_3. Finally, the decomposition of the binder $NiAl_2O_4$ as cycles proceed was also observed in studies performed on the oxygen carrier $NiO/NiAl_2O_4$. This work showed that the binder reacts with the fuel and therefore it can contribute to the modification of the oxygen carrier reactivity.

1. Introduction

To limit the increase of greenhouse gas emissions and stabilize climate at safe levels, CO_2 capture and sequestration technologies are nowadays being studied and developed [1]. Among these, Chemical Looping Combustion (CLC) has been suggested as an interesting alternative to conventional combustion to produce energy with inherent CO_2 capture [2,3]. CLC consists of an indirect combustion, where the oxygen needed for fuel oxidation is provided by a solid oxygen carrier. During this process, the fuel is first oxidized by the oxygen carrier and the latter is afterwards regenerated (re-oxidized) by air [4]. The most common CLC device consists of two interconnected fluidized beds ("combustion" and

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"regeneration" reactors) with a circulation of the solid oxygen carrier. However Noorman et al. [5,6] also proposed the possibility of working in a packed bed reactor where the oxygen carrier remains static and the different oxidation/reduction gas mixtures are alternatively injected. Gases produced in the combustion reactor are primarily CO_2 and H_2O. Thus, after water condensation, pure CO_2 is obtained and it can be directly stored or used. Outlet gases from the regeneration step (depleted air) can be directly emitted to the atmosphere. In conclusion, power generation by CLC technology does not require an energy intensive gas separation of CO_2 from exhaust gases, which is the most expensive step of CO_2 capture and sequestration.

Finding suitable oxygen carriers with sufficient reactivity, good mechanical properties and stability is strategic to increase the efficiency of CLC processes. Oxygen carriers are generally composed of an active phase (generally a metal oxide based on Ni, Fe, Cu, Mn or Co) and a porous binder (Al_2O_3, $NiAl_2O_4$, SiO_2, TiO_2, yttrium-stabilized zirconia, etc.), which provides higher surface area for reaction, mechanical strength and attrition resistance [7,8]. The final properties of the oxygen carrier (reactivity, mechanical strength, thermal and chemical stability, etc.) depend mainly on the metal oxide used, but also on the binder, as well as the preparation method. Several methods have been studied in the literature and can be classified in three groups:

- Mixing of metal oxide and binder powders (mechanical mixing [9,10], freeze granulation [11,12], spray drying [13,14], spin flash [15,16], etc.).
- Preparation by precipitation (co-precipitation [17,18], sol–gel [19,20], etc.).
- Preparation by impregnation (wet and incipient wetness impregnation, etc.) [21,22].

The freeze granulation is the most common preparation method at laboratory scale. However, only spray drying, spin flash and impregnation methods can be used at large scale for industrial production.

Numerous materials based on Ni, Fe, Cu, Mn and Co oxides have been studied and tested as oxygen carriers for CLC, at different working scales (laboratory and pilot scale) [7–10,17,21–35]. Among all these candidates, $NiO/NiAl_2O_4$ oxygen carrier is considered as a model oxygen carrier, due to its high reactivity and its good thermal stability. Indeed, it can work at high temperatures (900–1100 °C) owing to the high melting points of NiO and metallic Ni [7,9,17,23]. For these reasons Ni-based oxygen carriers are widely studied at laboratory scale, however their use should be minimized at industrial scale due to the high toxicity of this metal and health/safety issues.

Among all the possible metal oxide/binder combinations, some authors studied the use of γ-Al_2O_3 as a binder for NiO, but they observed that at high operating temperatures (>800 °C) the binder reacts with NiO to form $NiAl_2O_4$ [17,36,37]. $NiAl_2O_4$ is less reactive with fuel for CLC operations, although it can be partially reduced by the fuel [38]. Thus, the formation of $NiAl_2O_4$ reduces the amount of NiO able to deliver oxygen for combustion and so, the global performance of the oxygen carrier. To avoid the decrease of reactivity due to $NiAl_2O_4$ formation, Cho et al. [39] studied adding nickel in excess to get enough free NiO inside the particle and compensate for the loss of "reactive" nickel species. They showed that the initial NiO content must be very high (around 80 wt.%) to obtain a NiO free content of 60 wt.%. Gayán et al. [7] demonstrated that the formation of the spinel $NiAl_2O_4$ depends on the crystalline nature of the binder. They proposed to use a thermal treatment (at 1150 °C) to perform the phase transformation of γ-Al_2O_3 to α-Al_2O_3, in order to improve binder thermal stability. Results showed that the use of α-Al_2O_3 partially reduced the formation of $NiAl_2O_4$. Furthermore, Jin et al. [40] suggested to use $NiAl_2O_4$ directly as a binder instead of Al_2O_3. Afterwards, several authors studied the performances of the oxygen carrier $NiO/NiAl_2O_4$ and they generally observed high reactivity towards oxidation of different fuels (CH_4, syngas, etc.) and high stability. The reactivity of Al_2O_3 (used as binder) with NiO to form $NiAl_2O_4$ was studied by Adánez et al. [41] and Dueso et al. [36,42]. Adánez et al. [41] studied methane combustion (30 vol.% in N_2) in a CLC plant of 500 Wth during 100 h. The oxygen carrier used for this study was composed of 18 wt.% of NiO and 82 wt.% of α-Al_2O_3. They observed that α-Al_2O_3 reacted partially with NiO at high temperature to produce $NiAl_2O_4$. Moreover, their results revealed that both phases (NiO and produced $NiAl_2O_4$) could react with the fuel. Therefore, $NiAl_2O_4$ (used as binder or produced by reaction between NiO and the binder Al_2O_3) cannot be considered as an inert material in CLC processes: it is an additional source of oxygen for combustion [43]. The experiments also showed that the relative amount of free NiO in the oxygen carrier (after metal oxide NiO and binder Al_2O_3 reaction) depends on the oxygen carrier/fuel ratio (ϕ). Therefore, the production of $NiAl_2O_4$ decreased when ϕ decreased. Dueso et al. [36] performed thermogravimetric analyses simulating oxidation/reduction cycles with the same oxygen carrier (NiO/α-Al_2O_3) and CH_4 as fuel. They observed that the produced $NiAl_2O_4$ was less reactive than NiO. Furthermore, there was a direct relation between oxygen carrier conversion during the reduction step and the proportion of free NiO and $NiAl_2O_4$ present in the oxygen carrier after re-oxidation. 80% of nickel reduced in the previous cycle was reoxidized into free NiO while the rest was reoxidised into $NiAl_2O_4$ (fresh oxygen carrier composition: 18 wt.% NiO, 82 wt.% Al_2O_3; final composition: 14.4 wt.% NiO, 77 wt.% Al_2O_3 and 8.6 wt.% $NiAl_2O_4$). However, these authors have not studied the reactivity of the binder $NiAl_2O_4$ alone.

The stability of the nickel aluminate binder used in CLC is a very important parameter to ensure good mechanical strength of the oxygen carrier, and so, limit particles agglomeration and fragmentation which could damage the CLC process. In previous work [43], we studied the reactivity of the $NiAl_2O_4$ binder by performing oxidation/reduction cycles in a fixed bed reactor with CO as fuel. The major observation was that the binder underwent a structural modification, which modified its reactivity. X-ray Diffraction analyses showed that peaks related to $NiAl_2O_4$ were enlarged and shifted to wide diffraction angles. These results were explained by the gradual decomposition of $NiAl_2O_4$ to produce NiO and γ-Al_2O_3.

The purpose of the present work is to study the influence of the preparation method on the reactivity and stability of the binder $NiAl_2O_4$ and to quantify the amount of NiO produced by decomposition of the $NiAl_2O_4$ spinel phase during successive reduction/oxidation experiments.

The reactivity of two different binders was studied in a fixed bed reactor with CO as fuel. The evolution of both binders, in terms of reactivity and structural changes, was also investigated by the measurement of the amount of produced CO_2 during successive cycles. The materials were analyzed by X-ray Diffraction and Temperature Programmed Reduction to quantify the amount of NiO present in both materials before and after oxidation/reduction cycles. Additional tests were performed to compare the evolution of nickel aluminate in the binders and in the oxygen carrier ($NiO/NiAl_2O_4$).

2. Experimental section

2.1. Materials

Two $NiAl_2O_4$ binders were studied in this work. Cabot Corp. synthetized the first one (noted as B1) by spray pyrolysis of a mixture of nickel nitrate $Ni(NO_3)_2$ and gamma alumina γ-Al_2O_3