

Effects of Support on the Performance of NiO-Based Oxygen Carriers

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Résumé — Effets du support sur les performances de matériaux transporteurs d'oxygène à base d'oxyde de nickel — Les performances des matériaux transporteurs d'oxygène varient en fonction du support utilisé dans le procédé de combustion en boucle chimique. Différents matériaux à base d'oxyde de Nickel ont été synthétisés avec des concentrations élevées en NiO, comprises entre 60 et 70 %, sur différents supports (γ -Al₂O₃, pseudobohémite, α -Al₂O₃, γ -Al₂O₃ mélangée avec MgO, hydrotalcite, MgAl₂O₄ et γ -Al₂O₃ additivées avec du graphite) par mélange mécanique. Des tests de réactivité ont été conduits dans une thermobalance (ATG) à 950°C. Les matériaux supportés avec γ -Al₂O₃, γ -Al₂O₃ mélangée avec MgO, l'hydrotalcite et MgAl₂O₄ ont une capacité de transfert d'oxygène élevée et une réactivité élevée. L'addition de graphite dans l'alumine γ n'améliore ni la surface spécifique ni la réactivité. Avec la pseudo-bohémite, on observe une décroissance de la capacité de transfert d'oxygène et l'agglomération du matériau pendant la phase de réduction. L'ajout de MgO conduit à une baisse de la réactivité en réduction. Avec l'alumine α , la capacité de transfert est réduite. Les différences de réactivité peuvent être expliquées par les interactions entre NiO et le support, à partir d'analyses en réduction par température programmée. Les tests de réactivité conduits dans cette étude suggèrent que les supports à base de γ -Al₂O₃ et d'hydrotalcite sont les plus appropriés pour préparer les transporteurs d'oxygène contenant de l'oxyde de Nickel à haute concentration pour la combustion en boucle chimique.

Abstract — Effects of Support on the Performance of NiO-Based Oxygen Carriers — The performance of an oxygen carrier for Chemical Looping Combustion varies with the support material used. NiO oxygen carriers were prepared using 60 or 70 wt% NiO and different raw support materials (γ -Al₂O₃, pseudobohemite, α -Al₂O₃, γ -Al₂O₃ mixed with MgO, hydrotalcite, MgAl₂O₄, and γ -Al₂O₃ with added graphite) by the mechanical mixing method. Reactivity tests were conducted using a thermogravimetric analyzer (TGA) at 950°C. The oxygen carriers prepared using γ -Al₂O₃, γ -Al₂O₃ mixed with a small amount of MgO, hydrotalcite, and MgAl₂O₄ showed high oxygen transfer capacity, high oxygen utilization, and a high oxygen transfer rate. Graphite addition to γ -Al₂O₃ did not increase the surface area or reactivity. The use of pseudobohemite as a support led to a significant decrease in oxygen transfer capacity and severe agglomeration of the oxygen carriers during the redox reaction. The increase in MgO

content in the raw support materials decreased the reduction reactivity. The oxygen carriers prepared with $\alpha\text{-Al}_2\text{O}_3$ showed less oxygen transfer capacity than the other oxygen carriers. The differences in the reactivity according to the support type were explained by the relative strength of NiO-support interaction obtained from the temperature-programmed reduction analysis. The reactivity test results in this work indicate that $\gamma\text{-Al}_2\text{O}_3$ and hydrotalcite could be desirable raw support materials to prepare highly reactive NiO oxygen carriers with high NiO content.

NOTATION

Symbol

- X Degree of conversion
 m Mass of oxygen carrier (g)
 R_O Oxygen ratio

Greek symbol

- ω Mass-based conversion

Subscript

- ox* Fully oxidized state
red Fully reduced state

INTRODUCTION

Chemical Looping Combustion (CLC) is an emerging technology to mitigate carbon emission from fossil fuel power plants without a thermal efficiency loss. A CLC process consists of two inter-connected fluidized-bed reactors operated at high temperatures. An oxygen carrier composed of metal oxides and support materials supplies the oxygen required for the combustion of fuels in a Fuel Reactor (FR) and it is regenerated by receiving oxygen from the air in an Air Reactor (AR) (Fig. 1). High reactivity for the complete combustion of fuels is one of the important factors in the development of oxygen carriers because the oxygen carrier inventory and oxygen carrier circulation rate can be reduced.

The oxides of Ni, Fe, Cu and Mn have been frequently tested as potential active phase metal oxides [1-10]. Among these metal oxides, NiO has been preferred as the most appropriate metal oxide for the combustion of Natural Gas (NG) due to its high reactivity with NG and high oxygen ratio compared with other metal oxides, though it is more expensive and complete fuel conversion of CH_4 cannot be reached due to thermodynamic limitations. The metal oxides are supported on inorganic materials such as Al_2O_3 , ZrO_2 , TiO_2 , YSZ, etc. The supports improve the physical properties such as mechanical strength, surface area and porosity and increase the reactivity of oxygen carriers by promoting the dispersion of metal oxides. The supports also help to maintain the chemical and physical stability of the oxygen carriers.

However, the oxygen transfer capacity of the oxygen carriers decreases with the increase in support content. Some supports strongly interact with the active phase metal oxides and reduce the reactivity. From thermodynamic analysis, Mattisson *et al.* [11] reported that the presence of NiAl_2O_4 results in low methane conversion ($< 95.2\%$, $T > 900^\circ\text{C}$) to CO_2 and H_2O and increases the amounts of CO and H_2 in the gas outlet of a FR, while the conversion was higher for NiO ($> 99\%$ for $T < 900^\circ\text{C}$, 97.7% at $1\ 200^\circ\text{C}$). This means that increasing the amount of free NiO by reducing NiO-support

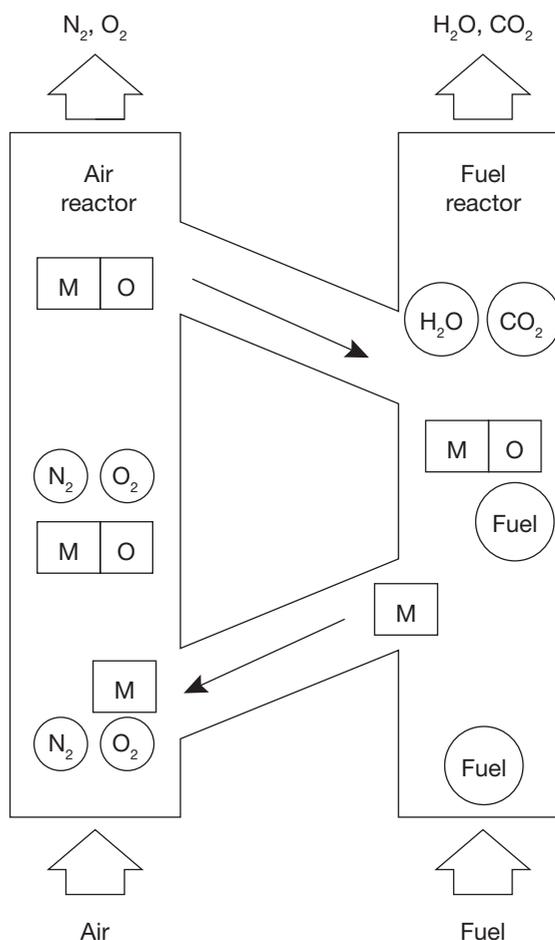


Figure 1

Schematic drawing of Chemical Looping Combustion process.
M: metal; O: oxygen.

interaction can lead to higher methane conversion to CO₂ and H₂O. Therefore, appropriate support material should be selected according to the metal oxide type used. The CH₄ conversion could also be enhanced by mixing the NiO with other metal oxides which do not have a restricted fuel conversion.

Several studies to screen the support materials for Ni are reported in the literature. Gayán *et al.* [7] used γ -Al₂O₃, α -Al₂O₃, MgAl₂O₄, γ -Al₂O₃ pre-coated with MgO, γ -Al₂O₃ pre-coated with CaO, and CaAl₂O₄ as the raw support materials for the preparation of NiO oxygen carriers. They reported that the Ni-based oxygen carrier prepared on γ -Al₂O₃ showed low reactivity and low methane combustion selectivity to CO₂ and H₂O due to the formation of NiAl₂O₄ by the interaction between NiO and γ -Al₂O₃, while the Ni-based oxygen carriers prepared on α -Al₂O₃, MgAl₂O₄ and CaAl₂O₄ showed high reactivity and high methane combustion selectivity to CO₂ and H₂O due to the decrease in the interaction between NiO and the supports. Their result was obtained for the maximum 38 wt% NiO. Ishida *et al.* [12] and Jin *et al.* [13] reported that an oxygen carrier with 60 wt% NiO supported on YSZ or NiAl₂O₄ showed high reactivity with methane and high regenerability. Shulman *et al.* [14] used commercially available NiO, α -Al₂O₃ and MgO to make spray-dried oxygen carriers with 40 wt% NiO supported on NiAl₂O₄, or 40 wt% NiO supported on NiAl₂O₄/MgAl₂O₄. The structurally stable raw support materials such as YSZ, NiAl₂O₄ and MgAl₂O₄ are commonly expensive and require higher calcination temperatures to obtain oxygen carriers with sufficient mechanical strength for an application to the fluidized-bed processes.

Although there have been lots of studies on the performance of NiO oxygen carriers, the performance of those with a NiO content of above 60 wt% supported on structurally less stable raw support materials such as pseudoboehmite, γ -Al₂O₃ or hydrotalcite is not well-known. Pseudoboehmite (AlOOH) is poorly crystalline boehmite. It is widely used as a binder material for the preparation of catalysts and solid sorbents. With the temperature increase, it changes to γ -Al₂O₃, θ -Al₂O₃, and then α -Al₂O₃, while losing H₂O. Hydrotalcite or Layered Double Hydroxide (LDH) is a layered material with positively charged layers and charge-balancing anions located in the interlayer region. The general form of hydrotalcite is [M²⁺_{1-x}M³⁺_x(OH)₂]_nAⁿ⁻_{x/n}, where M²⁺ and M³⁺ are Mg²⁺, Ca²⁺, Ni²⁺, etc. and Al³⁺, V³⁺, Fe³⁺, etc., and Aⁿ⁻ is generic anions compensating charge (CO₃²⁻, Cl⁻, OH⁻, SO₄²⁻, etc.). When the temperature increases, hydrotalcite is thermally decomposed and evolves gases such as H₂O and CO₂, and finally yields a mixture of divalent metal oxide (M²⁺O) and mixed metal spinel (M²⁺M³⁺O₄) [15, 16].

In this study, NiO oxygen carriers designed with high NiO content and various support materials (γ -Al₂O₃, pseudoboehmite, α -Al₂O₃, γ -Al₂O₃ mixed with MgO, hydro-

talcite, MgAl₂O₄, and γ -Al₂O₃ with added graphite) were prepared by the mechanical mixing method to investigate the effect of each support on the reactivity of oxygen carriers with high NiO content above 60 wt%. γ -Al₂O₃, pseudoboehmite and hydrotalcite are structurally less stable than α -Al₂O₃, MgAl₂O₄, YSZ and NiAl₂O₄. Although strong interactions between NiO and these structurally less stable raw support materials may be formed during calcination, it was assumed that the interaction could be reduced at a high NiO content because a lower number of support molecules would interact with a NiO molecule compared with a low NiO content. Furthermore, the surface area of these structurally less stable raw support materials is much higher than that of stable raw support materials. Therefore, performance improvement by a higher surface area after calcination was expected. The positive effects on the methane conversion caused by adding small amounts of MgO to α -Al₂O₃ for NiO oxygen carriers have been reported in the literature [14, 17-20]. This work investigated the effect of MgO addition on the reactivity of a NiO oxygen carrier prepared with γ -Al₂O₃. Hydrotalcite (Mg-Al LDH) was selected as a new raw support material containing a Mg component. α -Al₂O₃ and MgAl₂O₄ were tested for comparison purposes. Thermogravimetric analyzer (TGA) reactivity tests and Temperature-Programmed Reduction (TPR) were carried out to compare the oxygen transfer performance of the prepared oxygen carriers.

1 EXPERIMENTAL

1.1 Preparation of Oxygen Carriers

Oxygen carriers with high NiO content were prepared by the mechanical mixing method. Commercially available raw materials in powder form were used to prepare the oxygen carriers. The property data on the raw materials used in this work are given in Table 1. The NiO content was 60 or 70 wt%. γ -Al₂O₃, pseudoboehmite, γ -Al₂O₃ mixed with MgO, and hydrotalcite (Mg-Al LDH) were used as structurally less stable raw support materials. γ -Al₂O₃ mixed with additional 10 wt% graphite was tested to investigate if the reactivity could be improved by increasing the surface area of the oxygen carrier after burning out the graphite during calcination. The compositions of the oxygen carriers prepared in this work are presented in Table 2.

Raw materials were mechanically well mixed in pure water. The water content (usually 50 to 70 wt%) in the slurry was adjusted to make extrudable slurry. The slurry was extruded in a cylindrical form with 2-mm diameter and dried at 120°C. After calcination at 1 100°C for 5 h under an ambient air environment in a muffle oven, the oxygen carriers were crushed to obtain particles, with the particle size ranging from 106 to 150 μ m.

TABLE 1

Physical properties of raw materials used in oxygen carrier preparation

Raw material	Particle size (μm)	Surface area (m^2/g)
NiO	0.6 (d_{50}), 1.6 (max.)	
$\gamma\text{-Al}_2\text{O}_3$	5.6 (d_{50}), 12.9 (d_{90})	158
Pseudoboehmite	< 25 (78%), < 45 (98%)	234
$\alpha\text{-Al}_2\text{O}_3$	0.5 (d_{50}), 23.2 (d_{90})	9.1
MgO	3-8 (avg.)	45
Hydrotalcite	< 45 (51%), < 90 (92%)	250
MgAl_2O_4	1-5	0.9
Graphite	2.8 (d_{50}), 5.0 (d_{90})	2.5

The prepared oxygen carriers are designated by abbreviations implying a material name and a material content. N, GA, B, C, AA, M, HT and MA in the names of the oxygen

carriers mean NiO, $\gamma\text{-Al}_2\text{O}_3$, pseudoboehmite, graphite (carbon), $\alpha\text{-Al}_2\text{O}_3$, MgO, hydrotalcite and MgAl_2O_4 , respectively. For example, N70-GA-M8 means the oxygen carrier prepared with 70 wt% NiO and $\gamma\text{-Al}_2\text{O}_3$ mixed with 8 wt% MgO.

1.2 Reactivity Investigation in a TGA

The oxygen transfer capacity and reaction rate were measured with a TGA (Thermo Cahn, TherMax500) using 10 vol% methane in CO_2 and air as a reducing gas and an oxidizing gas, respectively, at the reaction temperature of 950°C and at ambient pressure. Approximately 20 mg of sample was placed on the alumina crucible and heated to the reaction temperature. The flow rate of the gases was $2.5 \times 10^{-6} \text{ m}^3/\text{s}$ on the basis of 0°C and 1 atm, at which external mass-transfer-limited reaction conditions could be avoided. An inert gas, N_2 , was fed into the reactor at the same flow rate after each reduction and oxidation period to prevent direct contact of the fuel gases and air. The weight and furnace temperature data were continuously recorded every second by a data acquisition unit. At least five cycles of reduction and oxidation were performed in the TGA for each oxygen carrier.

TABLE 2

Properties of oxygen carriers supported on different support materials

Oxygen carrier	Composition (solid raw material basis)		BET surface area** (m^2/g)	XRD**
	NiO (wt%)	Supports (wt%)		
N60-GA	60	$\gamma\text{-Al}_2\text{O}_3$ (40)	6.6	
N70-GA	70	$\gamma\text{-Al}_2\text{O}_3$ (30)	6.6	$\alpha\text{-Al}_2\text{O}_3$, NiO, NiAl_2O_4
N60-B	60	Pseudoboehmite (40)	5.1	$\alpha\text{-Al}_2\text{O}_3$, NiO, NiAl_2O_4
N70-B	70	Pseudoboehmite (30)	4.1	
N60-GA-C	60	$\gamma\text{-Al}_2\text{O}_3$ (40), graphite*	6.9	
N70-GA-C	70	$\gamma\text{-Al}_2\text{O}_3$ (30), graphite*	6.0	
N60-AA	60	$\alpha\text{-Al}_2\text{O}_3$ (40)	2.6	$\alpha\text{-Al}_2\text{O}_3$, NiO, NiAl_2O_4
N70-AA	70	$\alpha\text{-Al}_2\text{O}_3$ (30)	2.9	
N60-GA-M5	60	$\gamma\text{-Al}_2\text{O}_3$ (35), MgO (5)	9.9	
N60-GA-M10	60	$\gamma\text{-Al}_2\text{O}_3$ (30), MgO (10)	10.9	$\alpha\text{-Al}_2\text{O}_3$, NiO, NiAl_2O_4 , MgAl_2O_4
N70-GA-M4	70	$\gamma\text{-Al}_2\text{O}_3$ (26), MgO (4)	7.6	
N70-GA-M8	70	$\gamma\text{-Al}_2\text{O}_3$ (22), MgO (8)	8.7	
N60-HT	60	Hydrotalcite (40)	6.2	NiO, NiAl_2O_4 , MgAl_2O_4
N70-HT	70	Hydrotalcite (30)	5.5	
N60-MA	60	MgAl_2O_4 (40)	1.2	NiO, MgAl_2O_4
N70-MA	70	MgAl_2O_4 (30)	1.5	

* Graphite was additionally added at 10 wt%. ** Surface area and XRD analysis were conducted for the oxygen carriers calcined at $1\ 100^\circ\text{C}$.

When the reaction was very slow, reaction gases were changed to N₂ after 30 minute reaction. TPR tests were performed with the same TGA up to a temperature of 1 000°C (a temperature ramping rate of 5°C /min) using 10 vol% H₂ in Ar to investigate the interaction between NiO and supports and the reaction temperature zone.

The reactivity of each oxygen carrier at the fifth cycle was analyzed in terms of oxygen transfer capacity and oxygen transfer rate. Oxygen transfer capacity is the maximum percentage of mass change by oxygen transfer under the given experimental conditions, and it is calculated on the basis of the mass of the fresh oxygen carrier in its fully-oxidized state. The oxygen transfer rate is expressed as the mol of transferred oxygen per unit gram of oxygen carrier per unit time (mol O/g_{oc}/s). The degree of conversion, X , of a metal oxide is defined as:

$$X = \frac{m_{ox} - m}{m_{ox} - m_{red}} \quad (1)$$

where m is the instantaneous mass of an oxygen carrier measured by the TGA, and m_{ox} and m_{red} are the theoretical masses of the oxygen carrier in its fully-oxidized and fully-reduced state, respectively, when it is assumed that all oxygen in the NiO which was added as a raw material is transferable. The m_{ox} is equal to the mass of the fresh oxygen carrier in its fully-oxidized state. The denominator of Equation (1), the weight difference between m_{ox} and m_{red} , is the theoretical maximum amount of oxygen that can be transferred to the fuel. Oxygen utilization is percentage of the degree of conversion during the reduction reaction. A mass-based conversion, ω , was used to compare the mass change as a function of time. It is defined as

$$\omega = \frac{m}{m_{ox}} = R_O (X - 1) \quad (2)$$

The oxygen ratio (R_O), the theoretical maximum mass fraction of oxygen that can be transferred to the fuel, of pure NiO is 0.214. Therefore, the theoretical mass-based conversions of the prepared samples in their fully-reduced state are 0.87 and 0.85 for 60 and 70 wt% NiO content, respectively, on a dry solid raw material basis.

2 RESULTS AND DISCUSSION

2.1 Comparison of Oxygen Transfer Capacity, Oxygen Utilization and Oxygen Transfer Rate

The oxygen transfer capacities of the prepared NiO oxygen carriers are compared in Figure 2 as a function of the number of cycles. N60-HT and N70-HT showed the highest oxygen transfer capacities, 14.2 and 15.9 wt%, respectively. In the temperature-programmed desorption test for the raw hydro-

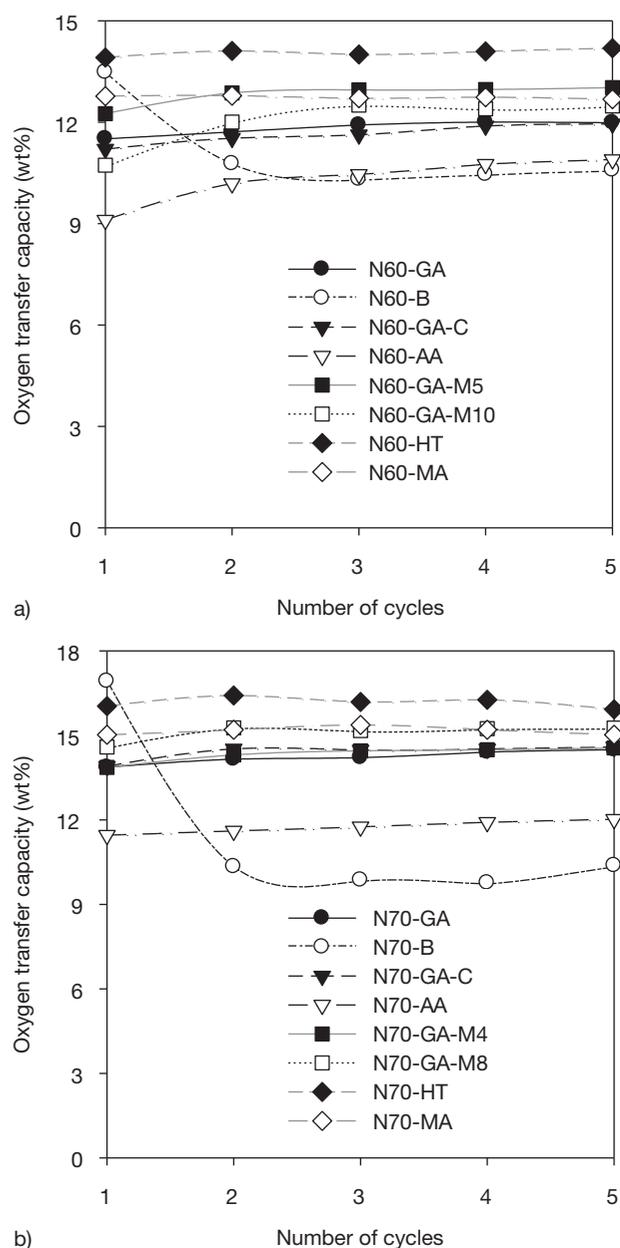


Figure 2

Oxygen transfer capacities of the oxygen carriers prepared using a) 60 wt% NiO and different raw support materials and b) 70 wt% NiO and different raw support materials.

talcite from room temperature to 1 000°C, weight loss of about 35 wt%, which was caused by dehydroxylation and decarbonation, was observed. This indicates that the NiO content of the oxygen carriers prepared using hydrotalcite would be increased after calcination compared with the initial NiO content in the raw materials. The oxygen transfer capacities of N60-HT and N70-HT are higher than expected, which could be ascribed to this increased NiO content.

Oxygen carriers prepared with γ - Al_2O_3 , γ - Al_2O_3 mixed with MgO , and MgAl_2O_4 also had high oxygen transfer capacities, above 12.0 and 14.5 wt% for 60 and 70 wt% NiO content, respectively. This means that more than 93 and 96% of the total oxygen in the 60 and 70 wt% NiO, respectively, were transferred to the fuel. The addition of graphite to γ - Al_2O_3 -based oxygen carriers did not affect their oxygen transfer capacity. When γ - Al_2O_3 mixed with MgO was used as a raw support material, the oxygen transfer capacity slightly increased. N60-AA and N70-AA showed relatively low oxygen transfer capacity compared with that of the oxygen carriers prepared with other raw support materials. This was an unexpected result because a stable support has been known to reduce the interaction between the metal oxide and support and increase oxygen transfer performance.

The oxygen transfer capacity of N60-B and N70-B decreased significantly from the second cycle and these oxygen carriers were not ever fully regenerated to the initial oxidation state after 30 minutes oxidation. This seems to be due to the sintering of NiO supported on pseudoboehmite during the redox cycle. After redox cycle tests, severe agglomeration was observed. The H_2 -TPR analysis for the fresh N60-B and N60-B after cyclic redox tests showed that the onset temperature of reduction was lowered a little and the total weight loss and the weight loss above 700°C were apparently reduced after cyclic redox tests (Fig. 3). X-Ray Diffraction (XRD) analysis for both fresh and cycle-tested N60-B showed that there was no tendency to NiAl_2O_4 increase after cyclic redox tests, as shown in Figure 4. On the basis of TPR and XRD

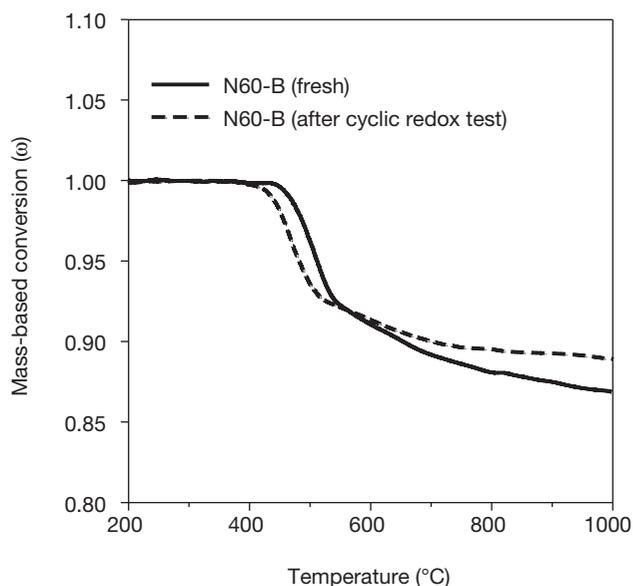


Figure 3

H_2 -TPR of the NiO oxygen carrier prepared using pseudoboehmite as a raw support material.

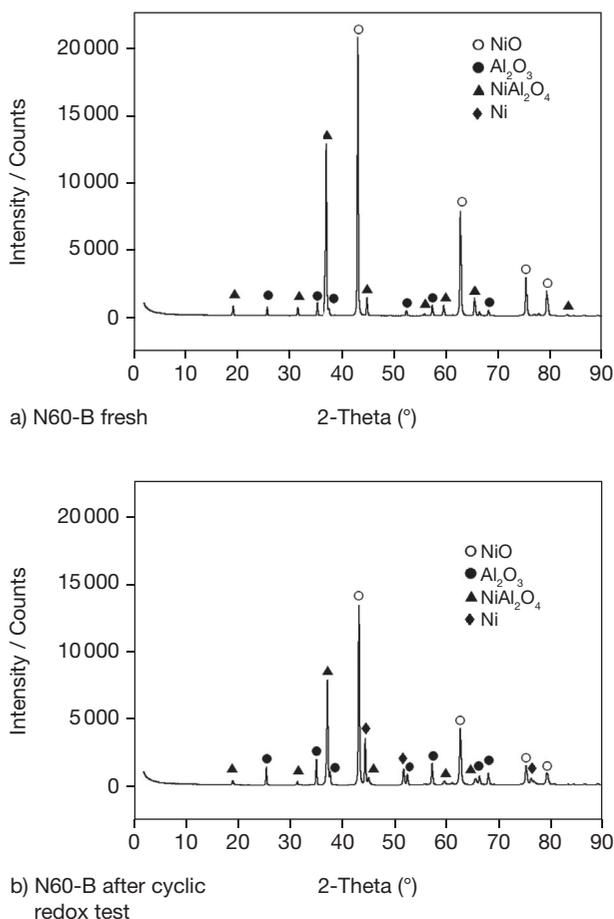
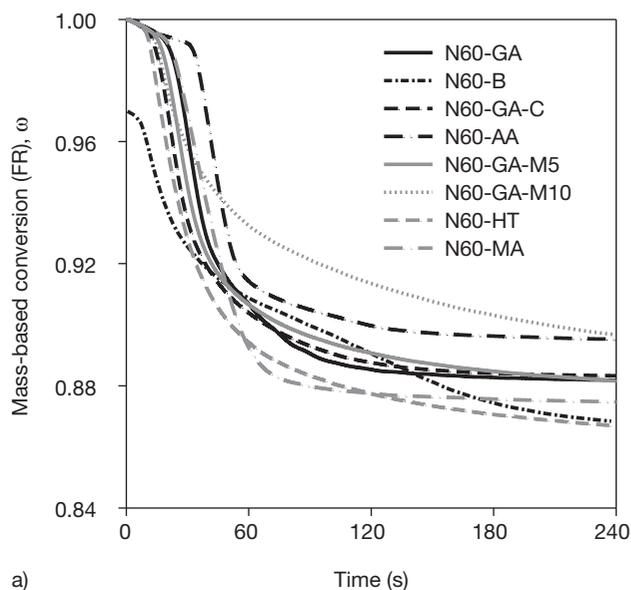


Figure 4

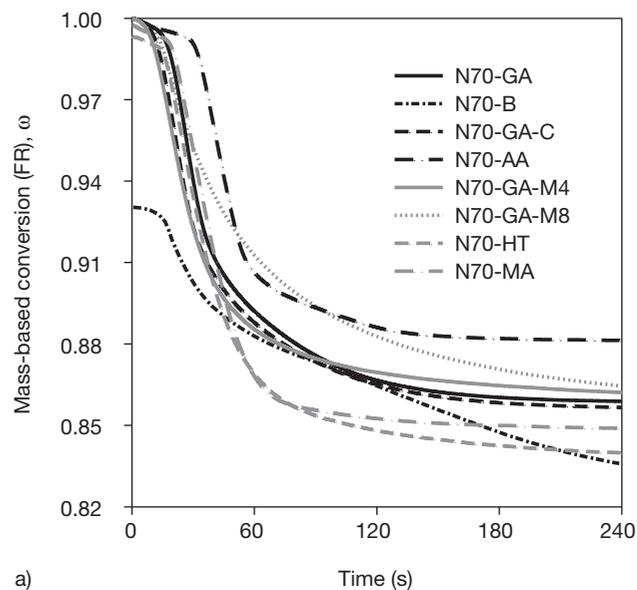
XRD results of a) fresh sample and b) the sample after cyclic redox tests at 950°C for the NiO oxygen carrier prepared using pseudoboehmite as a raw support material.

analysis, it can be concluded that the low reactivity of the NiO oxygen carrier prepared using pseudoboehmite was caused by sintering of NiO during the cyclic redox reaction. This means that the use of pseudoboehmite only as a support is not suitable.

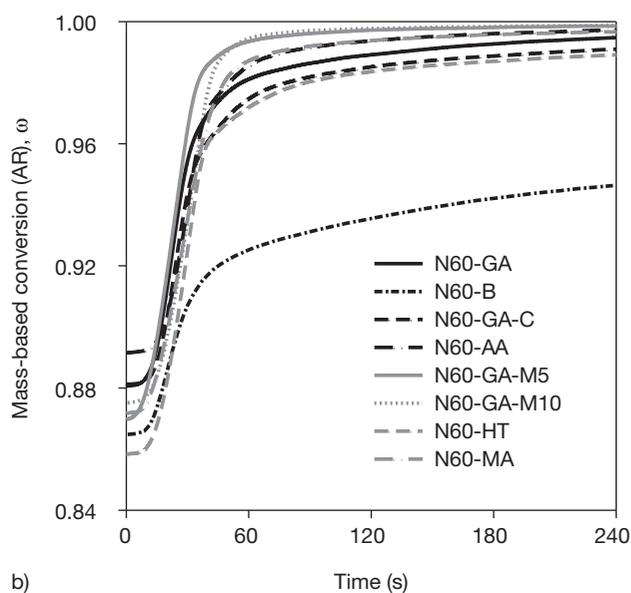
Mass-based conversion changes as a function of the reaction time in the fuel reactor and the air reactor are presented in Figures 5 and 6. N60-GA and N70-GA showed relatively fast reduction and oxidation. There was no apparent improvement in the reaction rate by graphite addition, which was anticipated from the result of the graphite addition not leading to the expected increase in the surface area, as shown in Table 2. N60-B and N70-B reacted very slowly in both reduction and oxidation due to the sintering of NiO, as explained above. Oxygen carriers containing a Mg component are reported to have the effects of enhancing the fuel combustion efficiency and reducing the agglomeration



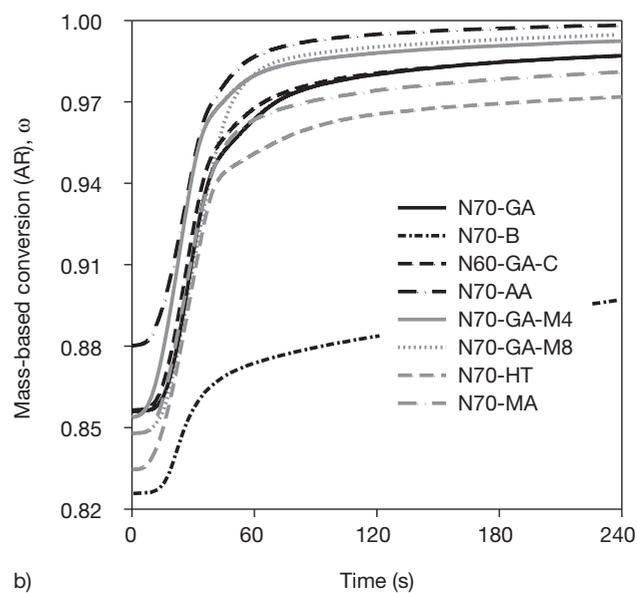
a)



a)



b)



b)

Figure 5

Mass-based conversion as a function of reaction time in a) the Fuel Reactor and b) the Air Reactor for the oxygen carriers prepared using 60 wt% NiO and different raw support materials.

Figure 6

Mass-based conversion as a function of reaction time in a) the Fuel Reactor and b) the Air Reactor for the oxygen carriers prepared using 70 wt% NiO and different raw support materials.

between particles [18, 21]. In this work, Mg was added using three different raw materials, MgO, MgAl₂O₄ and hydrotalcite. When a small amount of MgO (4 and 5 wt% for 60 and 70 wt% NiO content, respectively) was mixed with γ -Al₂O₃, the reactivity slightly increased. However, when the MgO content increased to 8 and 10 wt% for 60 and 70 wt% NiO content, respectively, the reduction slowed down signifi-

cantly, while the oxidation was faster than that of the other oxygen carriers. On the contrary, oxygen carriers prepared using MgAl₂O₄ and hydrotalcite showed relatively fast reduction and slow oxidation. Oxygen utilization changes of the oxygen carriers during reduction are presented as a function of reaction time in Figure 7. One minute after the beginning of the reduction, the oxygen utilization of N60-HT,

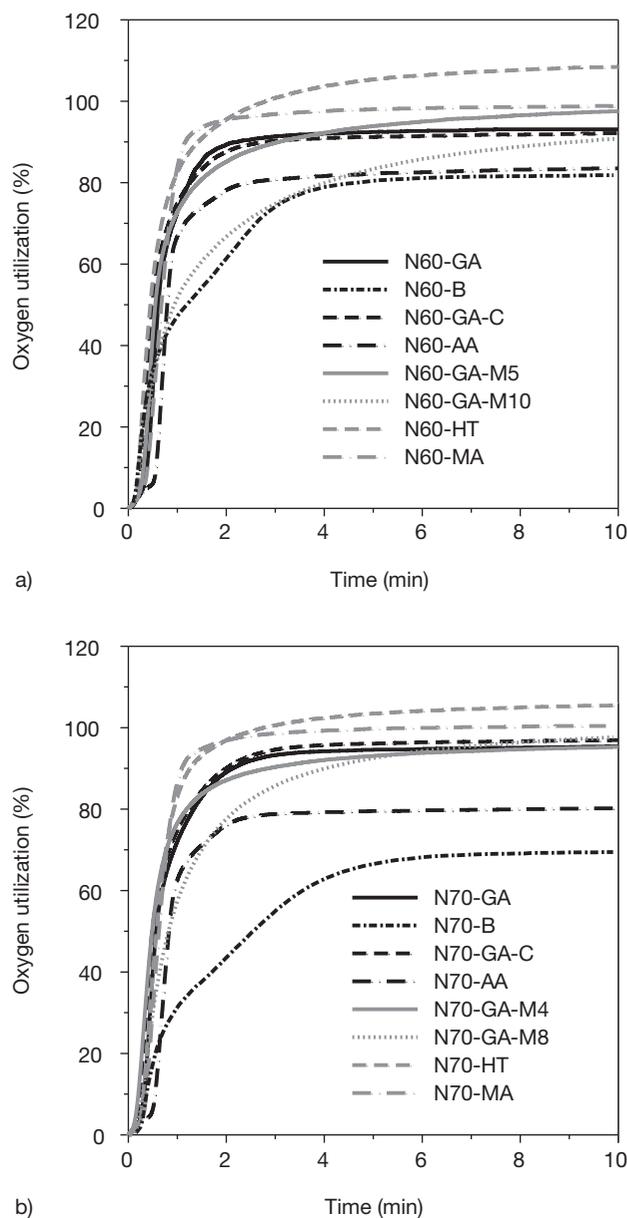


Figure 7

Oxygen utilization as a function of reaction time during reduction for the oxygen carriers prepared using (a) 60 wt% NiO and different raw support materials and (b) 70 wt% NiO and different raw support materials.

N70-HT, N60-MA and N70-MA was over 80% and the oxygen utilization of N60-GA, N70-GA, N60-GA-C, N70GA-C, N60-GA-M5, and N70-GA-M4 was over 70%. Oxygen carriers supported on pseudoboehmite, α -Al₂O₃ and γ -Al₂O₃ mixed with a large amount of MgO showed low oxygen utilization.

Oxygen transfer rate changes as a function of the degree of conversion for reduction and oxidation are presented in Figures 8 and 9. In an actual CLC process, an oxygen carrier circulates between the air reactor and the fuel reactor in a partially reduced state. The difference in degree of conversion between the air reactor and the fuel reactor is usually under 0.2. Therefore, it is important to circulate the oxygen carrier near the degree of conversion at which the highest reaction rate can be obtained. The highest reaction rate appeared in the degree of conversion (X) between 0.3 and 0.6 for reduction and between 0.5 and 0.8 for oxidation. In these ranges of degree of conversion, oxygen carriers prepared using γ -Al₂O₃, γ -Al₂O₃ mixed with a small amount of MgO, and hydrotalcite showed a high reaction rate at both reduction and oxidation and at both 60 and 70 wt% NiO content. Oxygen carriers supported on pseudoboehmite and γ -Al₂O₃ mixed with a large amount of MgO showed a very low oxygen transfer rate in the entire range of degree of conversion.

NiO oxygen carriers supported on γ -Al₂O₃ and calcined at 1 000-1 100°C [7] were described to have low reactivity and low oxygen utilization as a result of the strong interaction between the NiO and the support material. However, the reactivity analysis in this work showed that a NiO oxygen carrier supported on γ -Al₂O₃ also had high reactivity when a high NiO content was used although NiAl₂O₄ was formed by the NiO-support interaction during calcination as shown in the XRD analysis results (Tab. 2). γ -Al₂O₃ mixed with a small amount of MgO and hydrotalcite appeared to be also good supports for the preparation of highly reactive oxygen carriers with a high NiO content. To clarify the effect of the use of high NiO content, NiO oxygen carriers with 22 and 42 wt% NiO were prepared using γ -Al₂O₃ as a support, and N70-GA was calcined at 1 400°C. H₂-TPR analysis and redox cycle tests were conducted for these oxygen carriers. As shown in Figure 10, a large amount of oxygen in the oxygen carriers prepared with 22 and 42 wt% NiO was not transferred to the fuel until the temperature reached 900°C. The portions of the unreacted oxygen in the total oxygen until 900°C were about 60, 42, 19, and 4.6% for the oxygen carriers with 22, 42, 60, and 70 wt% NiO content, respectively. This indicates that the interaction between NiO and the support was reduced at a high NiO content. N70-GA calcined at 1 400°C transferred a smaller amount of oxygen than N70-GA calcined at 1 100°C. This also indicates that Al₂O₃ in the N70-GA calcined at 1 100°C did not completely interact with NiO to form stable NiAl₂O₄. XRD analysis also showed that alumina in the oxygen carriers prepared using γ -Al₂O₃ still remained as the α -Al₂O₃ form without being transformed completely into NiAl₂O₄. The result of cyclic redox tests at 950°C for these oxygen carriers confirms the effect of the use of high NiO content (Fig. 11). The oxygen utilization of N22-GA was only 27%, while that of N70-GA was 96%. This implies that the use of high NiO content could increase oxygen utilization. N70-GA calcined at 1 400°C was reduced

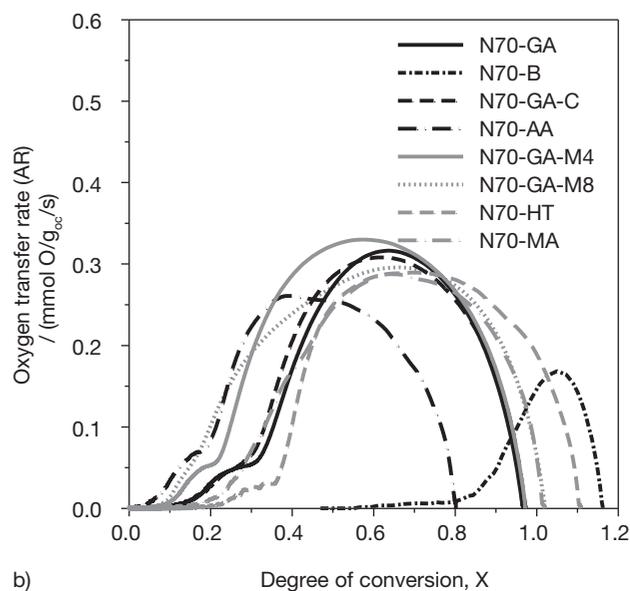
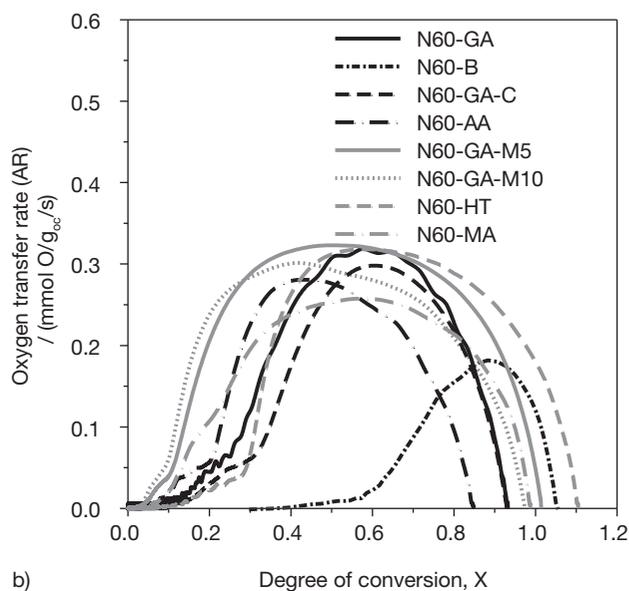
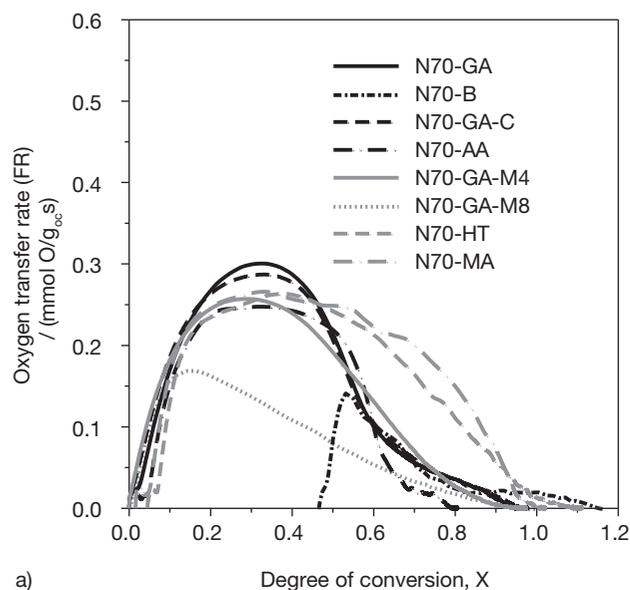
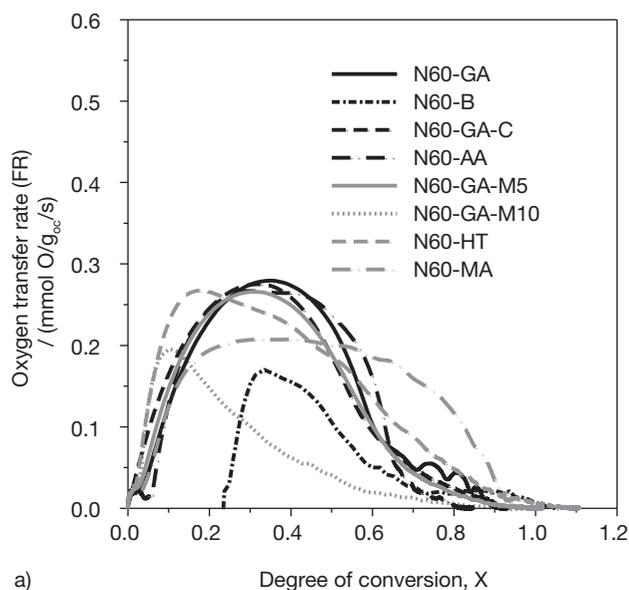


Figure 8

Oxygen transfer rate as a function of degree of conversion in a) the Fuel Reactor and b) the Air Reactor for the oxygen carriers prepared using 60 wt% NiO and different raw support materials.

Figure 9

Oxygen transfer rate as a function of degree of conversion in a) the Fuel Reactor and b) the Air Reactor for the oxygen carriers prepared using 70 wt% NiO and different raw support materials.

very slowly and its oxygen utilization was 77%, which indicates that a less strong interaction between NiO and Al_2O_3 can be achieved by the use of a high NiO content.

2.2 NiO-Support Interaction Study by TPR Analysis

To explain the differences in reactivities of the prepared oxygen carriers, H_2 -TPR tests were performed for fresh oxygen

carriers and the results are presented in Figure 12. The oxygen carriers prepared using the $\gamma\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$ with added graphite, and pseudoboehmite transferred most of their oxygen under 700°C , where free NiO is primarily reduced. NiO which interacted strongly with support materials transferred its oxygen to the fuel in a higher reaction temperature zone.

N60-GA-C and N70-GA-C were reduced in the lowest reaction temperature zone. It appeared as if graphite addition

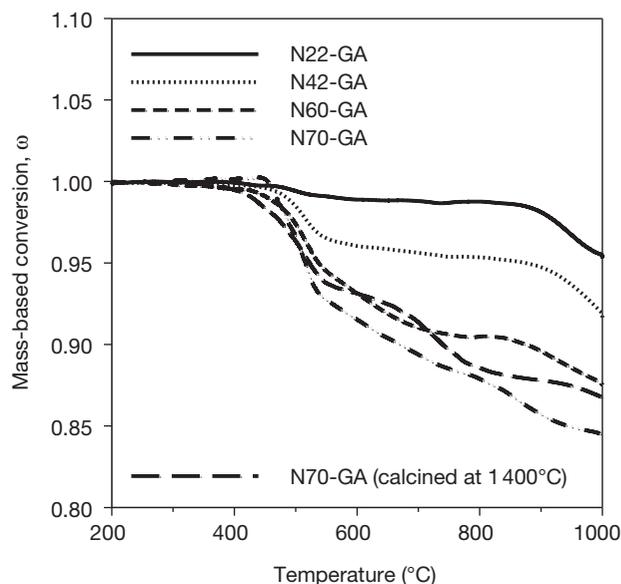


Figure 10

H₂-TPR of the fresh oxygen carriers prepared using different NiO contents and γ -Al₂O₃.

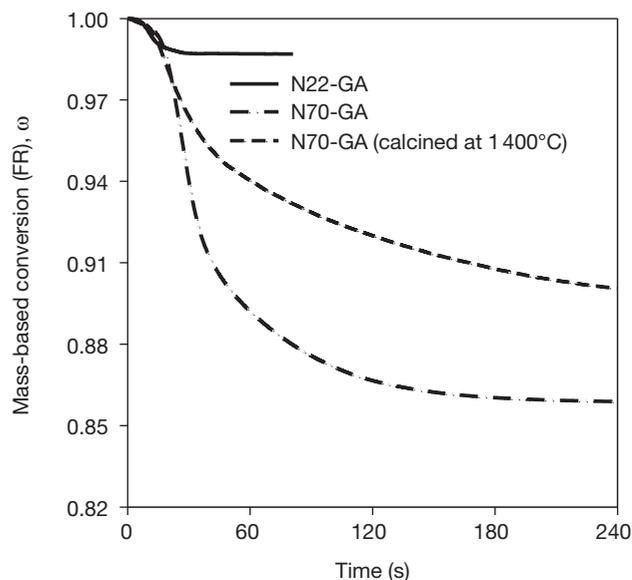
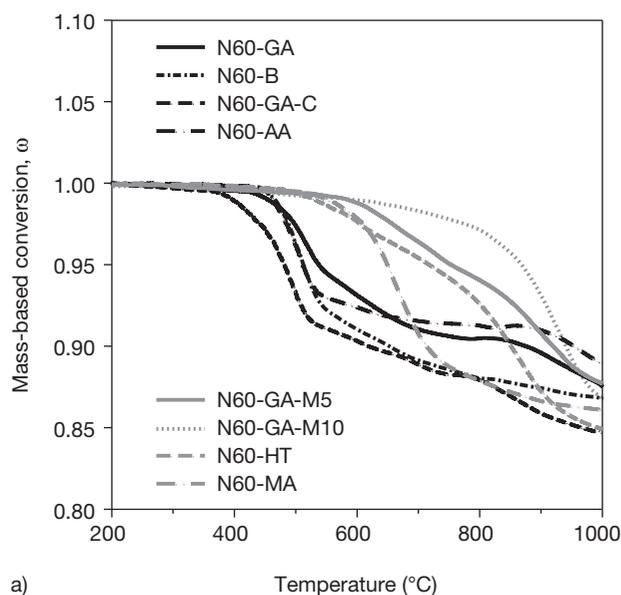
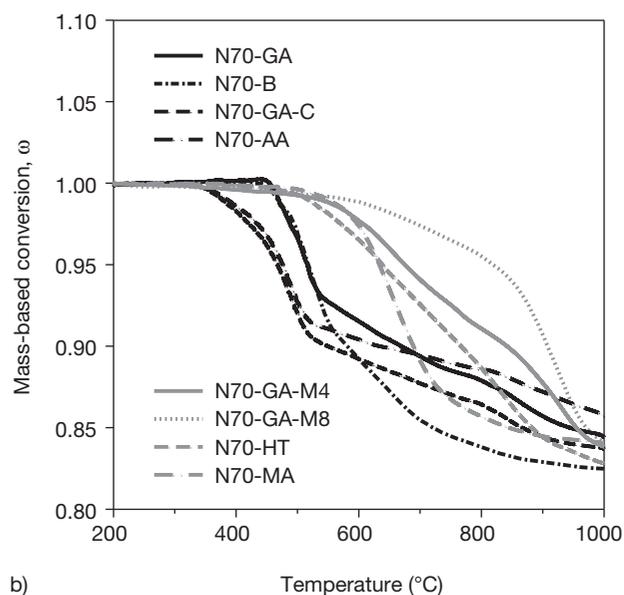


Figure 11

Mass-based conversion as a function of reaction time for the oxygen carriers prepared using NiO (NiO content: 22 and 70 wt%) and γ -Al₂O₃.



a)



b)

Figure 12

H₂-TPR of the fresh oxygen carriers prepared using a) 60 wt% NiO and different raw support materials and b) 70 wt% NiO and different raw support materials.

was effective for the reduction of the NiO-support interaction. However, in the TGA reactivity analysis there were no apparent differences in reactivity whether graphite was added or not. The discrepancy between TPR analysis and the TGA reactivity analysis seems to be caused by the fact that the initial structure of the fresh N60-GA-C and N70-GA-C became

similar to the structure of N60-GA and N70-GA during the cyclic redox reaction. This was confirmed by the fact that N60-GA-C and N70-GA-C showed apparently higher reactivity in the reduction of the first cycle than N60-GA and N70-GA, respectively.

TPR analysis for the fresh N60-B and N70-B seems to indicate low NiO-support interaction. However, they appeared to agglomerate severely during cyclic redox tests and reactivity decreased considerably from the second cycle, as described in the TGA reactivity analysis. Compared with the N60-GA and N70-GA, N60-AA and N70-AA transferred oxygen in a lower temperature zone at the beginning stage of reduction and transferred more oxygen under 700°C. However, in the temperature zone over 700°C, the weight reduction of the N60-AA and N70-AA was smaller than that of the N60-GA and N70-GA. To confirm this phenomenon, new oxygen carriers were prepared using different α -Al₂O₃ obtained by calcining the γ -Al₂O₃ at 1 200°C for 6 h. The H₂-TPR test results for the new oxygen carriers showed almost the same reduction profiles. TPR analysis for the oxygen carriers supported on α -Al₂O₃ is in agreement with the TGA reactivity analysis, which showed low oxygen transfer capacity.

The oxygen carriers containing a Mg component were reduced at a higher temperature zone, indicating that NiO-support interaction was enhanced by the addition of Mg. The oxygen carriers prepared using γ -Al₂O₃ mixed with a large amount of MgO required a higher reaction temperature to transfer the same amount of oxygen to H₂, indicating the highest NiO-support interaction. This result is consistent with the slow reduction of N60-GA-M10 and N70-GA-M8 in the TGA reactivity analysis. The oxygen carriers supported on hydrotalcite and MgAl₂O₄ transferred more oxygen at a lower reaction temperature zone than the oxygen carriers prepared using γ -Al₂O₃ mixed with MgO, which implies that lower NiO-support interaction could be achieved by the use of hydrotalcite and MgAl₂O₄. This is also consistent with the TGA analysis showing fast reduction of N60-HT and N60-MA compared with N60-GA-M5 and N60-GA-M8, and fast reduction of N70-HT and N70-MA compared with N70-GA-M4 and N70-GA-M8.

CONCLUSIONS

NiO-based oxygen carriers were prepared by the mechanical mixing method using high NiO content (60 or 70 wt%) and different support materials (γ -Al₂O₃, pseudoboehmite, α -Al₂O₃, γ -Al₂O₃ mixed with MgO, hydrotalcite, and MgAl₂O₄) to investigate the effect of each support on the reactivity. All oxygen carriers except for the ones prepared using pseudoboehmite and α -Al₂O₃ showed high oxygen transfer capacity, transferring more than 90% of the oxygen in the NiO added as a raw material. The oxygen carriers prepared using γ -Al₂O₃, γ -Al₂O₃ mixed with a small amount of MgO, and hydrotalcite showed a high reaction rate at both reduction and oxidation. From the comparison of the reactivity of the oxygen carriers, it may be concluded that γ -Al₂O₃ and hydrotalcite could be desirable raw support materials to

obtain highly reactive NiO oxygen carriers with high NiO content. In our future work, oxygen carriers for fluidized-bed applications will be prepared on a large scale by the spray-drying method using high NiO content and the selected support materials (γ -Al₂O₃, γ -Al₂O₃ mixed with MgO, and hydrotalcite), and their physical properties and reactivity will be evaluated.

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