Phase Interactions in Ni-Cu-Al₂O₃ Mixed Oxide Oxygen Carriers for Chemical Looping Applications

Jijiang Huang<sup>a</sup>, Wen Liu<sup>a</sup>,<sup>*</sup>, Wenting Hu<sup>b</sup>, Ian Metcalfe<sup>b</sup>, Yanhui Yang<sup>c</sup>,<sup>*</sup>, Bin Liu<sup>a</sup>,<sup>*</sup>

<sup>a</sup> School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459, Singapore

<sup>b</sup> School of Engineering, Newcastle University, Merz Court, Newcastle upon Tyne, NE1 7RU, United Kingdom

<sup>c</sup> Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Jiangsu National Synergetic Innovation Center for Advanced Materials, Nanjing Tech University, Nanjing 211816, China

<sup>*</sup> Corresponding Authors

E-mail addresses: wenliu@ntu.edu.sg (W. Liu), yhyang@njtech.edu.cn (Y. Yang), liubin@ntu.edu.sg (B. Liu).
Abstract

Chemical looping processes present great potentials to achieve carbon capture and fuel conversion with high thermodynamic efficiencies. Well-known applications of chemical looping include combustion and methane reforming, where phase interactions in oxygen carriers play important roles in determining the process performance. In this study, we systematically investigate the interactions between various phases in Ni-Cu-Al₂O₃ mixed oxides oxygen carriers, which were prepared from layered double hydroxides precursors, synthesized hydrothermally using urea and metal nitrates. It appears that the addition of 32 – 45 wt.% Al₂O₃ was sufficient to prevent sintering effects over 100 redox cycles at 800 °C, 1 atm, using methane as the fuel. The oxide phases and their compositions were determined using a set of complementary analytical techniques, allowing us to establish relationships between (i) the compositions of the mixed oxides, (ii) the chemical activity of the various types of lattice oxygen present and (iii) the distributions of gaseous products of chemical looping methane oxidation. We found that the mutual doping between NiO and CuO leads to enhanced lattice oxygen activities, whilst the solid solution of NiAl₂O₄ and CuAl₂O₄ leads to reduced lattice oxygen activity in the spinel phase, which also turns out to be particularly resistant to carbon deposition. The generality of the composition – activity - performance relationship is demonstrated by the successful prediction of the product distributions of methane oxidation based on solely the elemental compositions of the oxygen carriers. These findings enable the rational formulation of Ni-Cu-Al₂O₃ oxygen carriers for methane conversion with precise control of product selectivity.

Keywords: oxygen carriers, chemical looping combustion, methane conversion, phase interactions
1. Introduction

The term chemical looping represents a class of processes that uncouple conventionally homogeneous reactions into multiple steps, which may be carried out in separate reactors, using heterogeneous carriers to transfer the key species (e.g. oxygen) between the reactors. By doing so, the homogeneous reactants are never mixed, so that the products are in separate streams instead of a homogeneous mixture. Thus, the need for product separation is inherently absent [1], together with the associated high economic and environmental burdens [2]. Over the past two decades, chemical looping has been shown as a promising low carbon footprint alternative to conventional combustion [3], methane reforming [4] and water splitting processes [5]. In recent years, there have also been successes in demonstrating novel chemical looping applications in air separation [6], oxidative dehydrogenation of ethane [7] and epoxidation of ethylene [8].

Most known chemical looping applications involve redox reactions that exploit the chemical properties of the oxides of first row transition metals, e.g. Mn, Fe, Co, Ni and Cu [9]. The performance of a chemical looping process may be characterized by its efficiency in converting the feedstocks and the selectivity towards the desired products, e.g. CO\textsubscript{2} and H\textsubscript{2}O for combustion, CO and H\textsubscript{2} for reforming, etc. At a given temperature, a single oxide can only supply lattice oxygen \textit{(i.e. oxygen that is part of the metal oxide lattice rather than in the gas phase or some adsorbed forms) at specific $p_{O2}$ values, as mapped by Luo et al. [10], limiting it to a specific application with a constrained operation regimes. To overcome this limitation, researchers turned to mixed oxide oxygen carriers, the lattice oxygen activity of which can be tuned by their compositions.

A commercially viable oxygen carry must retain its reactivity over large numbers of redox cycles above 800 °C. However, redox active single oxides generally have strong tendencies to
sinter and are prone to attrition. These shortcomings significantly shorten the lifetimes of single oxide oxygen carriers. Hence, there is a generic need to introduce an secondary phase, typically oxides with higher melting points and attrition strength, to stabilize the oxygen carriers. Thus, oxygen carriers are almost always in the form of mixed oxides. Here, the term “mixed oxide oxygen carriers” broadly include three types of systems, viz. (i) physical mixtures (ii) solid solutions and (iii) ternary oxide compounds.

Physical mixtures correspond to composites in the absence of any bulk chemical interaction between the constituent oxides. The synergetic effects in physical mixtures typically arise from the multifunctional nature of the composites. Examples include CaO-CuO carriers for an integrated chemical looping combustion – calcium looping process [11], Cu modified Fe$_2$O$_3$ for methane reforming with minimal carbon deposition [12], and Fe$_2$O$_3$-ZrO$_2$ for chemical looping water splitting with enhanced lattice oxygen diffusion [13].

In a solid solution system, two or more iso-structural oxides form a single phase, in which the occupancies of the cationic sites are determined by the bulk cationic composition. The activity of the lattice oxygen in the solid solutions can be fine-tuned by the occupancies of the cationic sites. Examples of solid solution systems exploited for chemical looping processes include the Mn-Fe-O system for tuning the operating temperature of chemical looping with oxygen uncoupling (CLOU) [14] and the Mg-Ni-O system for enhanced sintering resistance over chemical looping combustion cycles [15].

Ternary compounds, such as spinel [16,17], perovskite [18,19], and brownmillerite [20] structured materials, can be produced by mixing metal oxides of specific oxidation states and cationic radii. Phase changes in the ternary oxide compounds often lead to drastic changes to the activity of the lattice oxygen [21]. For example, perovskite structured oxides are often capable of
supplying highly active lattice oxygen [22], whereas the brownmillerite structured compounds give rise to chemically stable lattice oxygen [23,24].

As discussed above, the activity of the lattice oxygen strongly depends on the chemical nature of the mixed oxides systems. Therefore, one needs to thoroughly understand the interactions within the mixtures in order to efficiently optimize the formation of high performance oxygen carriers for chemical looping applications.

Amongst all single metal oxygen carriers, NiO and CuO have the highest oxygen carrying capacities, which are 21 and 20 wt.%, respectively. NiO is an excellent oxygen carrier for methane reforming, but performs poorly in chemical looping methane combustion owing to the metallic Ni’s catalysis of carbon deposition [25]. CuO provides the most active lattice oxygen for combustion amongst all binary candidates [26]. However, CuO suffers from severe sintering owing to the low Tammann temperatures of CuO, Cu₂O and Cu [27]. Attempts to utilize CuO-NiO mixtures as oxygen carriers were made by Adánez and co-workers, who prepared the mixed oxides by impregnating CuO and NiO on α-Al₂O₃ or γ-Al₂O₃ supports [28,29]. The researchers concluded that NiO and NiAl₂O₄ could provide additional sintering resistance to CuO. However, these earlier studies regarded the various components in the mixed oxides as distinct phases (e.g. CuAl₂O₄, NiAl₂O₄, etc.), overlooking any possible phase interaction that may arise from the mixing (e.g. of CuAl₂O₄ and NiAl₂O₄) and the associated chemical consequences. Other researchers have reported synergetic effects between metallic Ni and Cu, when their mixtures are used for catalytic methane decomposition [30,31]. To date, the phase interactions in mixtures of NiO and CuO, in the presence of Al₂O₃, and the implications of these interactions in chemical looping processes, have not been addressed in the literature. This knowledge gap presents risks of misinterpretations and miscalculations of experimental
measurements, especially those taken from large-scale chemical looping systems. Accordingly, the focus of this work is to systematically investigate the phase interactions in a series of nickel-copper-alumina mixed oxides over chemical looping cycles. By understanding the chemistry and the redox properties of the Ni-Cu-Al₂O₃ system, we can propose formulations of oxygen carriers that may benefit specific chemical looping applications such as methane combustion and methane reforming.

2. Experimental

2.1. Preparation of oxygen carriers

NiO-CuO-Al₂O₃ were synthesized from Ni²⁺, Cu²⁺ and Al³⁺ containing layered double hydroxide (LDH) precursors, which facilitates the formation of equilibrium compositions upon calcination, owing to the atomic-level dispersion of Ni²⁺, Cu²⁺ and Al³⁺ ions in the brucite layers. The Ni/Cu/Al LDH precursors were prepared by hydrothermal syntheses, adapted from the procedure outlined by He et al. [32]. In a typical synthesis, stoichiometric amount of Ni(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O, Al(NO₃)₃·9H₂O and urea (the exact amount can be found in Appendix Table A1) were dissolved in 50 mL of deionized water in a 100 mL Teflon-lined stainless steel autoclave reactor. The concentration ratio of divalent cations (Cu²⁺ and Ni²⁺) to trivalent cations (Al³⁺) in the mixed solution was fixed at 3:1. The concentration of urea was 0.2 M. After hydrothermal reactions at 120 °C for 24 h, the resulting precipitates were extracted by centrifugation, washed with deionized water three times, and dried in air at 65 °C overnight. The dried precipitates were ground into powders for characterization and further processing. The mixed-oxide oxygen carriers were prepared by calcining the LDH precursors in a muffle furnace at 1000 °C (heating rate of 2 °C/min) for 6 h in air.
2.2. Characterization

The structure of the LDH precursors was studied by powder X-ray diffraction (XRD) in a Bruker AXS D8 diffractometer with filtered Cu Kα radiation (λ = 1.5406 Å) at 40 kV and 40 mA under ambient condition. The morphological information of the LDH precursors and the fresh oxygen carriers was examined by a field emission scanning electron microscopy (JEOL JSM 6700F). To study the phase compositions of the oxygen carrier samples before and after CLC cycles, synchrotron X-ray powder diffraction (SXRD) was performed on beamline ID22 at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The SXRD was undertaken in transmission geometry with an X-ray energy of 35.0 keV. Diffractograms were collected using a 9-channel Si 111 multi-analyzer stage detector at a scan rate of 0.8° min⁻¹.

2.3. Thermogravimetric analysis

The bulk compositions of the oxygen carrier samples were determined by thermogravimetric analysis (TGA/DSC2, Mettler Toledo), exploiting the fact that lattice oxygen associated with Cu²⁺, Ni²⁺ and Al³⁺ have drastically different activities even in the presence of phase interactions. In a typical analysis, ~10 mg of fresh oxide sample was first degassed by heating in N₂ from 50 °C at a rate of 10 °C/min to 700 °C, and then held isothermally for 120 min, followed by a temperature ramp to 1100 °C in N₂ at a rate of 10 °C/min and a dwell of 60 min, allowing all Cu(II) species (including those in CuO and CuAl₂O₄) to decompose to Cu (I) species (Cu₂O and CuAlO₂). The sample was subsequently exposed to 5 vol.% H₂ in N₂ at 900 °C for 180 min, to reduce all Cu(I) and Ni(II) (including those in NiO and NiAl₂O₄) to their corresponding metallic forms plus the residual Al₂O₃. Thus, the weight losses during the Cu(II) decomposition stage and the H₂ reduction stage can be used to deduce the mole fraction of Cu²⁺ and Ni²⁺ (according to Eq. A1 & A2), respectively. Lastly, the mole fraction of Al³⁺ is determined by oxygen balance.
The qualitative analysis of the activities of the lattice oxygen were performed by temperature programmed reduction (TPR) using the same TGA with the following program: (i) oxidation in air at 800 °C for 60 min, (ii) an isotherm in N2 at 100 °C for 10 min, and (iii) temperature ramp from 100 °C to 1000 °C at a rate of 5 °C/min in 5 vol.% H2 in N2. The TPR analysis was performed on the oxygen carrier samples before and after 100 redox cycles.

2.4. Chemical looping oxidation of methane

The activity of the lattice oxygen of the oxygen carriers over chemical looping cycles were characterized by the products of methane oxidation in an atmospheric pressure fixed-bed reactor, as shown schematically in Fig. 1. The apparatus has been described in the previous works by Huang et al. [15,33]. For each chemical looping experiment, 0.1 g of oxygen carrier was packed in a recrystallized alumina tube (99% purity) of I.D = 9 mm and wall thickness of ~1 mm. The packing arrangement, from top to bottom, is as follows: 8.8 g of white Al2O3 sand (1400 − 1700 μm), 0.1 g of oxygen carrier powder, 2.0 g of white Al2O3 sand (300−425 μm), 5.8 g of white Al2O3 sand (1400–1700 μm) and a plug of silica wool. The packed bed reactor was externally heated by a tubular furnace (MTF 10/15/130, Carbolite) and positioned such that the active bed (the oxygen carriers) was aligned to the center of the furnace’s heating zone. The length of the active bed (~ 1 mm) is one order of magnitude shorter than the length of the iso-temperature zone of the furnace (~ 3 cm), eliminating any axial temperature gradient across the active bed. Such a short bed is also expected to behave close to a differential reactor with minimal heat effects. The temperatures of the active bed were calibrated against the set point temperatures of the furnace under steady state operation prior to the chemical looping experiments. In each redox cycle, the feed gases were, consecutively: 1 min of N2 (purge), 5 min of 5 vol.% CH4/N2 (reduction), 1 min of N2 (purge), and 5 min of 5 vol.% O2/N2 (oxidation). The times chosen
allow the complete purge, reduction and oxidation of the active bed. The experiments were conducted isothermally at 800 °C for 100 redox cycles, whilst the gas flow rates were maintained at 225 mL/min (NTP) at all times by digital mass flow controllers (CS200-A, Sevenstar). The compositions of the effluent gases were measured using online gas analyzers (Caldos27, Uras26 and Magnos208, EL3020 series, ABB) at a sampling frequency of 1 Hz.

Fig. 1. Schematic of the fixed-bed for chemical looping study.

3. Results and discussion

3.1. Characterization of the LDH precursors

Fig. 2(a) – (e) show that all synthesized precursors exhibit flower-like morphologies with platelet assemblies (higher magnification images shown in Fig. A1). The SEM images also suggest that the sizes of the LDH crystallites increase with Cu content. The XRD patterns of the precursors, as shown in Fig. 2(f), confirm the successful synthesis of LDH, showing the characteristic (003) and (006) reflections at ca. 10° and 20°, respectively. For samples (1) – (4),
LDH is the only detectable crystalline phase in the precipitates. For sample (5), the additional peaks at ~12.9° and ~25.8° (Fig. A2) can be assigned to Cu$_2$(NO$_3$)(OH)$_3$ (PDF number 45-0594).

**Fig. 2.** SEM images (a-e) and XRD patterns (f) of the as-prepared Ni/Cu/Al LDHs with varying Ni/Cu/Al ratios. The molar ratio of (Ni$^{2+}$+Cu$^{2+}$):Al$^{3+}$ was fixed at 3:1, whereas the ratios of Ni$^{2+}$:Cu$^{2+}$ were (a) 3:0, (b) 2.5:0.5, (c) 2:1, (d) 1:2 and (e) 0:3, respectively. The diffraction patterns (i) – (v) correspond to the samples depicted in (a) – (e), respectively.

3.2. *Characterization of the fresh oxygen carriers*
Fig. 3. (a) Normalized sample mass as a function of time during N$_2$ decomposition and H$_2$ reduction. (b) First-order derivative of sample mass as a function of time. The black dash lines show the temperature profiles over time.

The elemental compositions of the oxide samples were estimated by isothermal thermogravimetric analyses (TGA). Fig. 3(a) shows the normalized weight loss curves, from which the compositions are quantified and presented in Table 1. From Table 1, it is apparent that the ratios of divalent cations to trivalent cations in the mixed oxides are less than the originally
intended 3:1. Thus, the oxygen carriers, calcined from the LDH precursors (1) – (5), are named based on the compositions determined by TGA, viz. Ni\(_{1.32}\)Al, Ni\(_{0.94}\)Cu\(_{0.46}\)Al, Ni\(_{0.32}\)Cu\(_{0.90}\)Al, Ni\(_{0.12}\)Cu\(_{0.71}\)Al and Cu\(_{0.80}\)Al, respectively. Indeed, the measured compositions are lower in Ni\(^{2+}\) and Cu\(^{2+}\) than what one would expect based on Table A1, viz. Ni\(_{3}\)Al, Ni\(_{2.5}\)Cu\(_{0.5}\)Al, NiCu\(_{2}\)Al, Cu\(_{2}\)NiAl and Cu\(_{3}\)Al, respectively. The discrepancy between the expectation and the measurements is attributed to the incomplete precipitation during the hydrothermal reactions. The total weight losses in TGA are taken to be the theoretical maximum oxygen transfer capacities (OTC), also shown in Table 1.

**Table 1.** The composition of various metal oxide samples, calculated from thermogravimetric analysis involving Cu(II) decomposition and Cu(I) and Ni(II) reduction.

<table>
<thead>
<tr>
<th>Oxygen carrier</th>
<th>Oxide basis (wt.%)</th>
<th>OTC mmol O/g</th>
<th>Nominal composition (mol.%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NiO</td>
<td>CuO</td>
<td>Al(_2)O(_3)</td>
</tr>
<tr>
<td></td>
<td>NiO</td>
<td>CuO</td>
<td>Al(_2)O(_3)</td>
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<tr>
<td></td>
<td>NiO</td>
<td>CuO</td>
<td>Al(_2)O(_3)</td>
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<tr>
<td></td>
<td>NiO</td>
<td>CuO</td>
<td>Al(_2)O(_3)</td>
</tr>
<tr>
<td></td>
<td>NiO</td>
<td>CuO</td>
<td>Al(_2)O(_3)</td>
</tr>
</tbody>
</table>

During the N\(_2\) decomposition (Fig. 3b), two differential thermogravimetry (DTG, *i.e.* the first time derivative of a weight loss curve) peaks can be seen. These two peaks correspond to the decomposition of CuO to Cu\(_2\)O and CuAl\(_2\)O\(_4\) to CuAlO\(_2\), respectively [34]. The DTG peak corresponding to CuAl\(_2\)O\(_4\) decomposition decreases in size with increasing Ni content. Specifically, the CuAl\(_2\)O\(_4\) content in the five samples can be ranked as Ni\(_{1.32}\)Al < Ni\(_{0.94}\)Cu\(_{0.46}\)Al <
Ni$_{0.32}$Cu$_{0.90}$Al < Ni$_{0.12}$Cu$_{0.71}$Al < Cu$_{0.80}$Al. This trend suggests that the measured amount of CuAl$_2$O$_4$ can be approximated by $n_{Al} - 2n_{Ni}$ or zero, whichever is larger, where $n_i$ corresponds to the stoichiometry in the samples’ names. In other words, Al$_2$O$_3$ reacts with NiO in preference to CuO to form NiAl$_2$O$_4$; any residual Al$_2$O$_3$ would then react with CuO to form CuAl$_2$O$_4$. Accordingly, the nominal chemical compositions of the oxygen carriers, not accounting for the formation of solid solutions, are calculated and shown in Table 1.

**Table 2.** Key parameters for the refinement of the SXRD patterns of the fresh oxygen carriers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>Lattice parameters</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>a (Å)</td>
</tr>
<tr>
<td>Ni$_{1.32}$Al</td>
<td>NiO</td>
<td>8.3541</td>
</tr>
<tr>
<td></td>
<td>NiAl$_2$O$_4$</td>
<td>8.0539</td>
</tr>
<tr>
<td>Ni$<em>{0.94}$Cu$</em>{0.06}$Al</td>
<td>NiO</td>
<td>8.3766</td>
</tr>
<tr>
<td></td>
<td>NiAl$_2$O$_4$</td>
<td>8.0567</td>
</tr>
<tr>
<td></td>
<td>CuO</td>
<td>4.6767</td>
</tr>
<tr>
<td>Ni$<em>{0.32}$Cu$</em>{0.90}$Al</td>
<td>CuO</td>
<td>4.6775</td>
</tr>
<tr>
<td></td>
<td>(Ni,Cu)Al$_2$O$_4$</td>
<td>8.0598</td>
</tr>
<tr>
<td>Ni$<em>{0.12}$Cu$</em>{0.71}$Al</td>
<td>CuO</td>
<td>4.6867</td>
</tr>
<tr>
<td></td>
<td>(Ni,Cu)Al$_2$O$_4$</td>
<td>8.0721</td>
</tr>
<tr>
<td>Cu$_{0.80}$Al</td>
<td>CuO</td>
<td>4.6888</td>
</tr>
<tr>
<td></td>
<td>CuAl$_2$O$_4$</td>
<td>8.0799</td>
</tr>
</tbody>
</table>
Fig. 4. SEM images of the fresh oxygen carriers, namely (a) Ni$_{1.32}$Al, (b) Ni$_{0.94}$Cu$_{0.46}$Al, (c) Ni$_{0.32}$Cu$_{0.90}$Al, (d) Ni$_{0.12}$Cu$_{0.71}$Al, and (e) Cu$_{0.80}$Al. (f) SXRD diffraction patterns of the fresh oxygen carriers, incident beam energy = 35 keV.

Fig. 4(a) – (e) depicts the morphologies of the freshly calcined oxygen carriers. It can be seen that the flower-like platelet morphologies of the LDH precursors persist after calcination. The SEM images also reveal signs of agglomeration and fracture of the platelets, probably as results of sintering and thermal stress during the calcination. Fig. 4(f) shows the SXRD patterns of the freshly prepared oxygen carriers. All diffraction peaks can be fully indexed by Rietveld refinement. The key refinement results are summarized in Table 2, listing the major phases present: NiO (halite structure), alumina spinel (Ni$_x$Cu$_{1-x}$Al$_2$O$_4$, with $0 \leq x \leq 1$) and CuO (tenorite
structure). In Ni_{0.32}Cu_{0.90}Al and Ni_{0.12}Cu_{0.71}Al, the NiO diffraction peaks are absent, suggesting that the majority of the Ni^{2+} should be present in the form of NiAl_{2}O_{4}. The lattice parameters calculated from the refined diffraction patterns indicate that the NiO lattice expands in the presence of CuO, whilst the CuO lattice shrinks in the presence of NiO. These changes show that the NiO and CuO in the oxygen carriers are substitutionally doped by one another [35]. However, the relatively low mutual solubility between NiO and CuO means that the halite phase and the tenorite phase could still be chemically represented by NiO and CuO, respectively. It should be noted that, in the present oxides system, the NiO phase may also be doped by Al^{3+} (as discussed in Section 3.4 below), making it practically impossible to quantify the composition of the individual phases using Vegard’s law.

TPR in 5% H_{2} (balanced by N_{2}) was performed by TGA to characterize the redox-active lattice oxygen (RALO) in the samples. Fig. 5 shows the weight loss curves during the TPR, normalized based on the initial mass, and the corresponding DTG curves. For Ni_{1.32}Al, the DTG peaks at 441, 562 and 816 °C can be assigned to the loss of RALO from NiO with weak NiO-Al_{2}O_{3} interaction, NiO with intermediate NiO-Al_{2}O_{3} interaction, and NiAl_{2}O_{4}, respectively [36]. It appears, as discussed in Section 3.4 below, that the intermediate NiO-Al_{2}O_{3} interaction is associated with the substitutional doping of Al^{3+} in NiO, which is inherently different from the “strong interaction” between NiO and Al_{2}O_{3} to form NiAl_{2}O_{4}. In the case of Cu_{0.80}Al, the two peaks at 272 and 432 °C can be explained by the loss of RALO from CuO and CuAl_{2}O_{4}, respectively. Based on the reference cases above, the DTG peaks for the mixed oxide samples (viz. Ni_{0.94}Cu_{0.46}Al, Ni_{0.32}Cu_{0.90}Al and Ni_{0.12}Cu_{0.71}Al) are be assigned to the reduction of CuO (243~265 °C), CuAl_{2}O_{4} (~510 °C), NiO (335 °C) and NiAl_{2}O_{4} (>800 °C). The compositions
identified by the TPR experiments are in agreement with the results of the isothermal TGA and SXRD, confirming the preferred formation of NiAl$_2$O$_4$.

**Fig. 5.** Normalized weight loss curves and their first-order time derivatives for temperature programmed reduction of the fresh oxygen carriers.
From Fig. 5, we observe that the DTG peaks associated with the reduction of CuO shift to lower temperatures with increasing Ni$^{2+}$ content. The same shifts are seen for the DTG peaks of NiO in the presence of increasing Cu$^{2+}$ content. It is generally expected that a TPR peak at low temperature corresponds to high RALO activity and vice versa. Therefore, the shifts of the CuO and NiO DTG peaks suggest that the RALO in both phases becomes more active owing to mutual doping. On the other hand, the DTG peaks corresponding to the reduction of the spinel compounds (CuAl$_2$O$_4$ and NiAl$_2$O$_4$) in the mixed oxide samples shifted to higher temperatures compared to that of the unmixed ones (Ni$_{1.32}$Al and Cu$_{0.80}$Al), suggesting that the formation of the Ni$_x$Cu$_{1-x}$Al$_2$O$_4$ solution reduces the activity of the RALO in the respective spinel compounds. The same effect can be seen in the results reported by Gayán et al. [29], although the authors did not address the shift of the DTG peaks.

The characterizations so far suggest that mixing NiO and CuO promotes the activities of RALO in CuO and NiO, whereas mixing NiAl$_2$O$_4$ and CuAl$_2$O$_4$ hinders the RALO activities in CuAl$_2$O$_4$ and NiAl$_2$O$_4$. In addition, the A sites in the AB$_2$O$_4$ spinel phase appear to be preferentially occupied by Ni$^{2+}$. The practical implications of these phase interactions are discussed in the next section.

### 3.3. Chemical looping oxidation of CH$_4$

The oxidation of methane is chosen as the benchmark process to characterize the activity of the various types of RALO under chemical looping conditions. In the present experimental design, three regimes exist during the reaction between methane and the oxygen carriers: (i) combustion to CO$_2$ and H$_2$O, (ii) reforming to CO and H$_2$ and (iii) direct decomposition to carbon and H$_2$. The three regimes correspond to the availability of high activity RALO, low activity RALO and no RALO, respectively [37]. When combustion and reforming take place
simultaneously, the product mixture may also undergo the water-gas-shift reaction: \( \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \) [38].

Fig. 6. Mole fraction of gaseous products during chemical looping CH\(_4\) conversion with 5% CH\(_4\)/N\(_2\) at 800 °C at the 2\(^{nd}\) and 100\(^{th}\) cycle. (a) Ni\(_{1.32}\)Al, (b) Ni\(_{0.94}\)Cu\(_{0.46}\)Al, (c) Ni\(_{0.32}\)Cu\(_{0.90}\)Al, (d) Ni\(_{0.12}\)Cu\(_{0.71}\)Al and (e) Cu\(_{0.80}\)Al.
Fig. 6 shows the product composition profiles over time during the reactions with methane in the 2nd and 100th redox cycles. The steam mole fractions in the product were estimated based on hydrogen balance, knowing the mole fractions of CH₄ and H₂ in the product. In Fig. 6, the three reaction regimes are manifested by (i) a CO₂ peak and a H₂O peak with similar profile and twice the magnitude, (ii) a CO peak and a H₂ peak with similar profile and twice the magnitude (with the exception of Ni₁.₃₂Al and Ni₀.₉₄Cu₀.₄₆Al (Fig. 6 a-b) where the ratio of $p_{\text{H}_2}/p_{\text{CO}}$ exceeds 2 owing to an early onset of carbon deposition), and (iii) a tail of H₂ in the absence of other gaseous products, respectively. The gradual and successive transitions between the regimes suggest that more active RALOs are consumed first, in agreement with the observation by Adánez et al. [28]. A notable feature in Fig. 6(c) is the second CO₂ peak, which is succeeded by a CO peak. This second CO₂ peak corresponds to the combustion of the CO produced from methane reforming, as discussed by Cabello et al. [39]. Fig. 6 also shows that the product composition profiles of Ni₀.₉₄Cu₀.₄₆Al, Ni₀.₁₂Cu₀.₇₁Al and Cu₀.₈₀Al remain largely unchanged after 100 redox cycles, i.e. the phase changes due to redox reactions are reversible. In contrast, Ni₁.₃₂Al and Ni₀.₃₂Cu₀.₉₀Al produce significantly different product compositions between the second cycle and the 100th cycle; these variations are further discussed in the next section.

The overall product distribution of methane oxidation in each cycle are represented by the conversion of methane and the yields of CO, CO₂ and carbon, as plotted in Fig. 7, which confirms the stable performance of Ni₀.₉₄Cu₀.₄₆Al, Ni₀.₁₂Cu₀.₇₁Al and Cu₀.₈₀Al over 100 cycles. Meanwhile, the redox cycles have made Ni₁.₃₂Al more selective towards CO with reduced yields of CO₂ and carbon. Ni₀.₃₂Cu₀.₉₀Al appears to be self-activating, producing more CO₂, CO and carbon over cycles.
A few correlations between the nominal chemical compositions of the oxygen carriers (as shown in Table 1) and their initial performance can be observed. Firstly, samples containing halite structured NiO (viz. Ni$_{1.32}$Al and Ni$_{0.94}$Cu$_{0.46}$Al) yield significantly more carbon and convert more methane than ones without NiO. This is owing to the fact that the reduced Ni catalyzes the direct decomposition of CH$_4$ to carbon and H$_2$ [40]. Secondly, samples with higher Cu contents are more selective towards CO$_2$. Amongst the samples tested, Cu$_{0.80}$Al is the best for complete combustion, producing CO$_2$ close to 97% of the theoretical maximum yield (3.14...
mmol/gCuO) with negligible CO byproduct. This is in agreement with the general consensus that CuO is the most reactive oxygen carrier for chemical looping combustion of methane [41].

Thirdly, the samples with higher NiAl2O4 content (as estimated in Table 1) are associated with higher CO yield and lower CO2 yield, meaning that the RALO in NiAl2O4 favors methane reforming. Lastly, the presence of Ni1-xCuxAl2O4 seems to suppress carbon deposition in Ni0.12Cu0.71Al, resulting in even lower carbon yield than the benchmark formulation of Cu0.80Al. The low carbon yield could be attributed to the resilient RALO in Ni1-xCuxAl2O4, which oxidized any deposited carbon until all spinel phases are decomposed by reduction. Analogous carbon inhibition effect by FeAl2O4 has been discussed by Bao et al. [42].

![Graphs](image)

**Fig. 8.** (a-e) The reduction curves of different NiO-CuO-Al2O3 oxygen carriers in selected cycles: 2nd, 10th, 20th, 50th and 100th and (f) solid conversion during reduction with 5% CH4/N2.

The total availability of RALO under chemical looping conditions is characterized by solid conversion (according to Eq. A3), for which unity corresponds to the case that all RALO
participates in redox reactions. The evolution of solid conversion versus time curves for the five oxygen carriers at selected cycles are plotted in Fig. 8(a) – (e), respectively. Fig. 8(f) shows the total solid conversion achieved by the end of each methane oxidation over 100 redox cycles. In Fig. 8(f), it can be seen that > 80% solid conversion is achieved for all five samples, indicating high oxygen carrying capacities and the absence of any bulk deactivation phenomenon (e.g. sintering). For Ni_{0.32}Cu_{0.90}Al, the total solid conversion increases cyclically; this may be explained by the changes in RALO activity, as discussed in the next section.

Based on the results above, an attempt is made to correlate the chemical compositions of the samples (as shown in Table 1) to the product distributions (as shown in Fig. 7). We crudely postulate that all CuO, CuAl_2O_4 and NiO can fully oxidize CH_4 to CO_2 and H_2O, whereas NiAl_2O_4 only partially oxidizes CH_4 to CO and H_2. The amount of RALO participating in the methane oxidation is estimated based on the solid conversion reported in Fig. 8(f). Additionally, the yield of carbon is assumed to be proportional to the amount of NiO present. The product yields of the freshly calcined oxygen carriers, estimated based on the assumptions above, are compared to the measured values in Fig. 9(a), which shows that the proposed correlation can roughly predict the product compositions. Notable discrepancies in Fig. 9(a) include the overestimated CO_2 yields and the underestimated CO yields, both suggesting that some of the CuAl_2O_4 and NiO participated in methane reforming instead of combustion. The experimental observations so far are be summarized by the schematic depicted in Fig. 9(b).
Fig. 9. (a) Measured product yields in the second cycle versus the product yields predicted based on the compositions of the fresh oxygen carriers. The yields are calculated based on the total mass of active oxides (CuO and NiO). The diagonal line corresponds to exactly accurate prediction. (b) A schematic diagram of the reaction sequence.

In the present chemical looping experiments, the effect of RALO promotion by the mutual doping between CuO and NiO, as suggested by the TPR results, is not apparent. This is probably because the reduction of CuO and NiO during the looping cycles at 800 °C are too fast to be rate limiting. However, this promotion effect presents opportunities for exploitation for low temperature chemical looping applications, such as exhaust gas oxidation [43] and membrane assisted steam methane reforming [44]. Another major phase interaction observed in the mixed
oxide system is the solid solution of CuAl$_2$O$_4$ and NiAl$_2$O$_4$, which gave rise to RALO with high selectivity towards methane reforming and high resistance against carbon deposition.

Last but not least, it should be noted that the cycling experiments were performed under considerably dilute gas environments (viz. 5% CH$_4$ and 5% O$_2$ for reduction and oxidation, respectively) and in chemically short beds, as opposed to the ~100% CH$_4$ and air fed to the circulating fluidized beds systems that would be used in commercial-scale chemical looping systems. The chosen experimental conditions result in prolonged reactions periods in the absence of strong heat and mass transfer effects, enabling the measurements of key kinetic features (e.g. the three regimes of methane oxidation) as the lattice oxygen depletes over time. These measurements are critical to reactor modelling but cannot be achieved in a large-scale continuous system, which typically operates under equilibrium limited or mass transfer limited reaction regimes. On the other hand, the bench-scale set up is not useful in evaluating certain physical properties of the oxygen carriers, such as attrition and fluidization behaviors, which are also crucial to the process scale-up.

### 3.4. Phase compositions after chemical looping cycles

The oxygen carriers after 100 redox cycles were recovered and examined by SXRD and TPR. The SXRD patterns, as shown in Fig. A4) confirm that the phase compositions of Ni$_{0.94}$Cu$_{0.46}$Al, Ni$_{0.12}$Cu$_{0.71}$Al and Cu$_{0.80}$Al remain roughly the same after 100 redox cycles; this explains their stable performance. The SXRD patterns for Ni$_{1.32}$Al and Ni$_{0.32}$Cu$_{0.90}$Al, however, suggest changes in phase compositions, which should be responsible for the variation of their behavior over cycling.

Fig. 10(a) compares the SXRD and TPR results of Ni$_{1.32}$Al before and after 100 redox cycles. Fig. 10(a) shows that, the SXRD peaks of the post-cycling NiO shift to lower angles, whereas
those of NiAl₂O₄ shift to higher angles. This may be explained by a net transfer of dopant Al³⁺ from the NiO phase to the NiAl₂O₄ phase, as discussed by Elrefaie and Smeltzer [45]. Fig. 10(b) shows changes of the low temperature (< 450 °C) and intermediate temperature (> 530 °C) DTG peaks, which correspond to the reduction of NiO with weak (α-type) and intermediate (β-type) interaction with Al₂O₃, respectively. The enlargement of the α peak and the reduction of the β peak indicate that the interaction between NiO and Al₂O₃ is weakened; this could be correlated to the precipitation of Al³⁺ dopant from the NiO phase, as suggested by the SXRD results. The changes are also accompanied by a shift of the NiAl₂O₄ DTG peak from 816 to 871 °C. In chemical looping systems, Al³⁺ doping usually leads to lower RALO activity [46]. Thus, the DTG peak shifts, in conjunction with the SXRD results, indicate that a portion of the substitutional dopant Al³⁺ precipitated from the NiO phase during cycling. Furthermore, the reduction in the carbon yield (shown in Fig. 7d) suggests that some of the precipitated Al₂O₃ reacted with NiO, forming additional NiAl₂O₄, which also gave rise to the reduced CO₂ yield and the increased CO yield, as shown in Fig. 7(b)-(c).
Fig. 10. SXRD patterns (a & c) and TPR curves (b & d) of the fresh and spent Ni$_{1.32}$Al and Ni$_{0.32}$Cu$_{0.90}$Al.

Fig. 10(c) compares the SXRD and TPR results of Ni$_{0.32}$Cu$_{0.90}$Al before and after chemical looping cycles. In Fig. 10(c), the NiO SXRD peaks of the cycled sample indicate the precipitation of NiO from the originally halite-free Ni$_{0.32}$Cu$_{0.90}$Al. It should be noted that the sharp Al$_2$O$_3$ peak seen in Fig. 10(c) comes from the contamination by the inert packing material (alumina sand) used in the chemical looping experiments and should be regarded as an experimental artifact. In Fig. 10(d), the shift of the CuO DTG peak from 261 to 275 °C also suggests the precipitation of dopant NiO from CuO over redox cycles. The observed precipitations are in line with the phenomena described by Huang et al. [40], who validated the
effect of fast redox cycles on irreversible phase segregations of mixed oxides. The precipitated NiO in Ni$_{0.32}$Cu$_{0.90}$Al, albeit little, facilitated the increases in CH$_4$ conversion, CO$_2$ yield, CO yield and carbon yield, as shown in Fig. 7. In a commercial chemical looping process where more concentrated feedstocks (e.g. almost 100% methane) are used, the reaction time scales (i.e. the time taken for the oxygen carrier to go through one redox cycle) would be even shorter, meaning that the issue of phase segregation may become more severe.

4. Conclusions

In this investigation, the layered double hydroxides-derived mixed oxides contain between 32 and 45 wt% Al$_2$O$_3$ (prior to the formation of spinel), which provide the oxygen carriers with sufficient sintering resistance to maintain high oxygen carrying capacity (>80% of the theoretical maximum) over 100 redox cycles at 800 °C. However, there are substantial differences between their methane oxidation behaviors. For example, Ni$_{1.32}$Al shows selectivities towards CO$_2$ and CO of < 20% and > 60%, respectively, with severe carbon deposition; whereas Cu$_{0.80}$Al shows CO$_2$ and CO selectivities of ~90% and < 10%, respectively, with little carbon deposition (as shown in Fig A.3). The drastic differences in the selectivities and the product distributions can be explained by the differences in phase compositions.

In the Ni-Cu-Al-O mixed oxide system, three phases are present, viz. a halite phase (predominately NiO), a tenorite phase (predominately CuO) and a spinel phase (a solid solution of CuAl$_2$O$_4$ and NiAl$_2$O$_4$). In the spinel phase, NiAl$_2$O$_4$ is more stable than CuAl$_2$O$_4$. Therefore, in the case when Al$_2$O$_3$ is stoichiometrically limited, it would react preferentially with NiO. The mutual doping between NiO and CuO is also observed; this phenomenon gives rise to increased lattice oxygen activity in both phases. However, the formation of the spinel phase solid solution reduces the lattice oxygen activity. At 800 °C, the lattice oxygen in CuO, CuAl$_2$O$_4$ and
NiO are sufficiently active for the complete combustion of methane, whereas NiAl$_2$O$_4$ is highly selective towards methane reforming. On the other hand, the low activity of the lattice oxygen in NiAl$_2$O$_4$ makes it resistant to carbon deposition.

The correlation between the phase compositions and the product selectivities provides a convenient rule-of-thumb for predicting the product yields based on solely the elemental compositions of the oxygen carriers. This also means that the selectivity of the chemical looping process can be tuned by the chemical compositions of the Ni-Cu-Al-O mixed oxides. Based on our findings, we postulate that a highly reactive oxygen carrier for chemical looping combustion should consist of Ni$^{2+}$ doped CuO supported on Cu$^{2+}$ doped NiAl$_2$O$_4$, whereas a highly selective oxygen carrier for chemical looping reforming should consist of Cu$^{2+}$ doped NiAl$_2$O$_4$, possibly also promoted by small amount of CH$_4$ activation catalysts.

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**Notations**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>CLC</td>
<td>Chemical looping combustion</td>
</tr>
<tr>
<td>CLOU</td>
<td>Chemical looping with oxygen uncoupling</td>
</tr>
<tr>
<td>DTG</td>
<td>Differential thermogravimetry</td>
</tr>
<tr>
<td>I.D.</td>
<td>Inner diameter</td>
</tr>
<tr>
<td>LDH</td>
<td>Layered double hydroxides</td>
</tr>
<tr>
<td>NTP</td>
<td>Standard conditions for temperature and pressure, \textit{viz.} 20 \degree C, 1 atm.</td>
</tr>
<tr>
<td>OTC</td>
<td>Oxygen transfer capacity</td>
</tr>
<tr>
<td>RALO</td>
<td>Redox-active lattice oxygen</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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</table>
The composition of the NiO-CuO-Al₂O₃ oxygen carriers were studied using TGA, and the CuO and NiO mass fractions were calculated by the following equations:

\[
x_{\text{CuO}}(\text{wt}%) = \left(\frac{m_{\text{max}} - m_{\text{min,OU}}}{M_\text{CuO} \cdot m_{\text{max}}}ight) \times 100 \quad (A1)
\]

\[
x_{\text{NiO}}(\text{wt}%) = \left(\frac{(m_{\text{max}} - m_{\text{min,ro}} - 2\times(m_{\text{max}} - m_{\text{min,OU}}))}{M_\text{NiO} \cdot m_{\text{max}}}ight) \times 100 \quad (A2)
\]

where \(m_{\text{max}}\) is the sample mass after stabilization at 700 °C under \(N_2\) for 120 min; \(m_{\text{min,OU}}\) and \(m_{\text{min,ro}}\) are the sample mass at the end of the Cu(II) decomposition and H₂ reduction of Cu(I) and Ni(II); \(M_\text{O}\), \(M_\text{CuO}\) and \(M_\text{NiO}\) are the corresponding molar mass, respectively.

The oxygen carrier conversion during reduction with 5 vol.% CH₄ in \(N_2\) was calculated by:

\[
X_{\text{reduction}} = \frac{\left(N_{\text{CO}_2} \times 4 + N_\text{CO}\right) \cdot M_{\text{MeO}}}{m_0 \cdot x_{\text{MeO}}} \quad (A3)
\]

where \(N_{\text{CO}_2}\) and \(N_\text{CO}\) are the amount of CO₂ and CO out of the reactive bed; \(m_0\) is the sample mass; \(x_{\text{MeO}}\) (mass fraction of Ni/Cu oxides) was calculated from the fraction of NiO and CuO determined by TGA; and \(M_{\text{MeO}}\) (average molar mass) is the arithmetic average of \(M_{\text{NiO}}\) and \(M_{\text{CuO}}\) considering their mole fraction in the oxygen carrier.
Fig. A1. High magnification SEM images of the as-prepared Ni/Cu/Al LDHs for samples 2#-5#.
Fig. A2. Enlarged XRD pattern of the as-prepared Cu/Al LDH with 0.2 M urea as the precipitant via hydrothermal synthesis at 120 °C for 24 h.
Fig. A3. Selectivity of CO₂, CO, carbon and H₂ during oxygen carrier reduction with 5% CH₄ in 100 chemical looping cycles.
Fig. A4. SXRD patterns of different spent NiO-CuO-Al2O3 oxygen carriers.

Table A1. The preparation recipe (mmol) for the Ni/Cu/Al LDHs.

<table>
<thead>
<tr>
<th>S/N</th>
<th>Ni(NO3)2</th>
<th>Cu(NO3)2</th>
<th>Al(NO3)3</th>
<th>urea</th>
<th>Oxygen carrier notation</th>
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<tbody>
<tr>
<td>1</td>
<td>15</td>
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<td>5</td>
<td>10</td>
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</tr>
<tr>
<td>2</td>
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<td>2.5</td>
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<tr>
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<td>10</td>
<td>5</td>
<td>5</td>
<td>10</td>
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</tr>
<tr>
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<td>5</td>
<td>10</td>
<td>5</td>
<td>10</td>
<td>Ni0.12Cu0.71Al</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>15</td>
<td>5</td>
<td>10</td>
<td>Cu0.80Al</td>
</tr>
</tbody>
</table>
References


doi:10.1039/C2EE22801G.


