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## Inhibiting the interaction between FeO and Al<sub>2</sub>O<sub>3</sub> during chemical looping production of hydrogen

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Hydrogen of high purity can be produced by chemical looping using iron oxide as an oxygen carrier and making use of the reaction between steam and either iron or FeO. However, this process is viable only if the iron oxide can be cycled between the fully-oxidised and fully-reduced states many times. This can be achieved if the iron oxide is supported on refractory oxides such as alumina. Unfortunately, the interaction between alumina and oxides of iron to form FeAl<sub>2</sub>O<sub>4</sub> hinders the kinetics of the reactions essential to the production of hydrogen, *viz.* the reduction of Fe(II) to metallic iron by a mixture of CO and CO<sub>2</sub> prior to the oxidation by steam. Here, oxygen carriers containing Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> were doped with Na<sub>2</sub>O and, or, MgO, in order to inhibit the formation of FeAl<sub>2</sub>O<sub>4</sub> by forming NaAlO<sub>2</sub> or MgAl<sub>2</sub>O<sub>4</sub>, respectively. The performance of the modified oxygen carriers for producing hydrogen, *i.e.* cyclic transitions between Fe<sub>2</sub>O<sub>3</sub> (or Fe<sub>3</sub>O<sub>4</sub>) and metallic Fe at 1123 K were investigated. It was found that the interaction between FeO and Al<sub>2</sub>O<sub>3</sub> was successfully mitigated in an oxygen carrier containing Mg, with an Al: Mg ratio of 2, resulting in consistently stable and high capacity for producing hydrogen by chemical looping, whether or not the material was oxidised fully in air in each cycle. However, the oxygen carrier without Mg only remained active when a step to oxidise the sample in air was included in each cycle. Otherwise it progressively deactivated with cycling, showing substantial interaction between Al<sub>2</sub>O<sub>3</sub> and oxides of Fe.

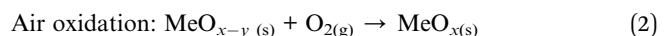
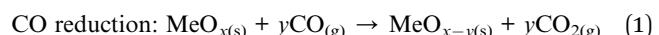
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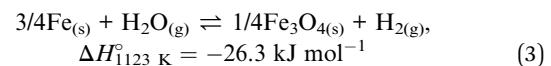
### 1. Introduction

Hydrogen is a potential fuel for a low-carbon economy, provided it can be manufactured with minimal release of CO<sub>2</sub> to the atmosphere. Generally, to generate hydrogen, carbonaceous fuels need to be consumed, usually *via* large-scale, energy-intensive processes such as steam-methane reforming. Where the hydrogen is to be used in polymeric-electrolyte-membrane fuel cells; an additional process is required to purify the hydrogen to avoid poisoning of the Pt electrodes by the low concentrations of CO which contaminate the product of steam-methane reforming.<sup>1</sup> However, CO may be less of a problem in other types of fuel cells, *e.g.* solid-oxide fuel cells or solid molten carbonate fuel cells.<sup>1</sup> An alternative process, capable of producing pure hydrogen directly from carbonaceous fuels, at small to medium scales with simultaneous capture of CO<sub>2</sub>, is chemical looping hydrogen production.<sup>2</sup>

Chemical looping techniques rely on the ability of transition metal oxides to transport oxygen from an oxidising environment to a reducing environment. When CO is used as a reductant and the oxygen in air is used as an oxidant, the reactions can be generalised:



where MeO<sub>x</sub> and MeO<sub>x-y</sub> represent the oxidised and reduced forms of the transition metal oxide, referred to here, together with any supporting matrix, as the oxygen carrier. In this example, oxygen is transported from air by MeO<sub>x</sub> to combust CO in a nitrogen-free environment, resulting in a stream of pure CO<sub>2</sub>, which is suitable for carbon storage. Here, the additional cost associated with the separation of CO<sub>2</sub> from N<sub>2</sub> for carbon capture in conventional coal-fired power plants is avoided. In a variant of the above, if iron oxide is used as an oxygen carrier, hydrogen can be produced during the oxidation stage of the steam-iron process:



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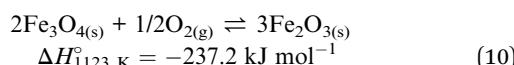
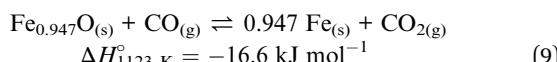
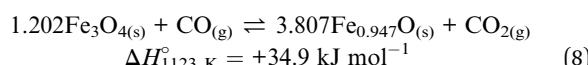
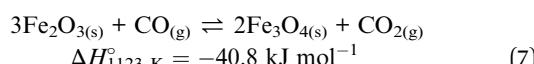
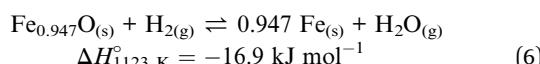
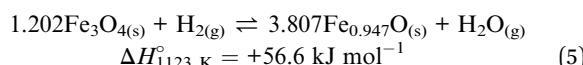
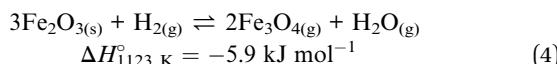
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originally patented by Messerschmitt.<sup>3</sup> Reed and Berg<sup>4</sup> proposed a system to produce pure hydrogen continuously using the steam–iron process, by circulating iron oxides between three interconnected fluidised bed reactors. In their process, the iron oxide oxygen carrier was subjected to repeated redox reactions, *i.e.* chemical looping. When synthesis gas, *e.g.* a mixture of CO and H<sub>2</sub> is used as a fuel, the reactions in the three-reactor system would be:



In the first reactor, *viz.* the fuel reactor, reactions (4)–(9) would be conducted, where haematite (Fe<sub>2</sub>O<sub>3</sub>) is reduced by CO and H<sub>2</sub> sequentially to magnetite (Fe<sub>3</sub>O<sub>4</sub>), wüstite (Fe<sub>0.947</sub>O) and iron (Fe). Both wüstite and iron can be then oxidised by steam in the second reactor, *viz.* the steam reactor, according to the reverse of reactions (3) and (5). The solid product, magnetite, is further oxidised to haematite according to the exothermic reaction (10), in the third reactor, *viz.* the air reactor, which provides heat to the system. Overall, the chemical energy of the synthesis gas is used to produce hydrogen by splitting water *via* chemical looping of the iron oxide. Of course, the hydrogen used during the reduction is mixed with CO, whereas the hydrogen produced in this manner is effectively free from carbonaceous contamination, and has high purity.<sup>2</sup>

One of the major challenges in the production of hydrogen by chemical looping is the development of a stable oxygen carrier capable of being reduced and oxidised over many cycles without deactivation. When almost pure iron oxide (99 wt% haematite) is used as an oxygen carrier, the reduction of Fe<sub>3</sub>O<sub>4</sub> to Fe in each cycle led to rapid deactivation within the first few cycles.<sup>2</sup> However, by limiting the extent of reduction to wüstite (FeO) in every cycle, a stable hydrogen yield could be obtained over more than 10 redox cycles.<sup>2</sup> Nevertheless, the transition between Fe and Fe<sub>3</sub>O<sub>4</sub> produces about four times as much hydrogen as the transition between wüstite (FeO) and magnetite (Fe<sub>3</sub>O<sub>4</sub>), for a given mass of iron, so that reduction to iron is desirable to maximise yield. Further studies have shown that supporting the iron oxide on Al<sub>2</sub>O<sub>3</sub> could stabilise the

performance of iron-based oxygen carriers.<sup>5–7</sup> However, it was also found that hercynite, FeAl<sub>2</sub>O<sub>4</sub>, was inevitably formed in the presence of Al<sub>2</sub>O<sub>3</sub> and this slowed down the rate of reduction of the supported iron oxide when the latter was reduced beyond Fe<sub>3</sub>O<sub>4</sub>.<sup>8</sup> Here, FeAl<sub>2</sub>O<sub>4</sub> belongs to the spinel group of crystalline phases with a general formula of AB<sub>2</sub>O<sub>4</sub>, where the A-sites are typically occupied by divalent cations and B-sites by trivalent cations. On the other hand, it was hypothesised by Kidambi *et al.*,<sup>7</sup> that the formation and destruction of solid phases on each redox cycle might be important in maintaining the activity of the oxygen carrier. However, Liu *et al.*<sup>9</sup> have demonstrated the stabilising effect of a ZrO<sub>2</sub> support on the performance of iron oxide oxygen carriers for chemical looping hydrogen production. The support in this system is chemically stable, and no phases involving iron oxide are formed. Therefore, albeit desirable, it is not strictly necessary for there to be changes of phase to promote a carrier's stability over many cycles. Nevertheless, one drawback of using ZrO<sub>2</sub> as a support material for chemical looping is its high cost relative to common refractory materials, *e.g.* Al<sub>2</sub>O<sub>3</sub>.

To avoid the formation of FeAl<sub>2</sub>O<sub>4</sub>, several researchers have proposed using MgAl<sub>2</sub>O<sub>4</sub> as a replacement for Al<sub>2</sub>O<sub>3</sub> as a support material on the basis that it prevents spinel formation with the transition metal oxides for chemical looping combustion operations.<sup>10–12</sup> It was found that the use of MgAl<sub>2</sub>O<sub>4</sub> (melting point = 2135 °C) as a support material gave both excellent mechanical strength and thermal resistance, whilst the reactivity of the active metal oxides for chemical looping combustion was preserved.<sup>10–12</sup> Interestingly, when CuO is used as a chemical looping agent, researchers have reported that the formation of the spinel phase CuAl<sub>2</sub>O<sub>4</sub> is inhibited in the presence of trace amounts of alkali metals (*e.g.* Na and K).<sup>13–15</sup> The source of these alkali metal “contaminants” is most likely to be the Na- and K-dawsonites, *viz.* NaAlCO<sub>3</sub>(OH)<sub>2</sub> and KAlCO<sub>3</sub>(OH)<sub>2</sub>, respectively, during the preparation of the oxygen carriers by co-precipitation.

The aim of the present study is to investigate the potential to use oxygen carriers containing a mixture of Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O and, or, MgO for producing hydrogen by chemical looping, because the use of Na<sub>2</sub>O and MgO could potentially inhibit the formation of FeAl<sub>2</sub>O<sub>4</sub> by forming NaAlO<sub>2</sub> and MgAl<sub>2</sub>O<sub>4</sub> with Al<sub>2</sub>O<sub>3</sub> instead. Two oxygen carriers were synthesised: one containing oxides of Fe, Al and Na and another containing oxides of Fe, Mg, Al and Na. Both oxygen carriers were investigated under conditions which simulate the production of hydrogen by chemical looping. The formation and interaction of different phases of mixed oxides during repeated redox cycling were studied using *ex situ* characterisation techniques.

## 2. Experimental

### 2.1. Preparation of oxygen carriers

The oxygen carriers containing (a) oxides of Fe, Al and Na, and (b) oxides of Fe, Mg, Al and Na are hereinafter referred to, respectively, as NAFO and NMAFO. Both oxygen carriers were synthesised using the method of co-precipitation with a slowly decreasing pH. In both cases, the precipitant used was an

aqueous solution containing NaOH ( $\geq 98$  wt%, Fisher Scientific) and Na<sub>2</sub>CO<sub>3</sub> ( $\geq 99.5$  wt%, Fisher Scientific) mixed at a molar ratio of 1 : 1 to give a total concentration of  $[\text{Na}^+] \sim 4$  M. The precursors were aqueous solutions containing nitrates of Mg<sup>2+</sup>, Al<sup>3+</sup> and Fe<sup>3+</sup>, *viz.* Mg(NO<sub>3</sub>)<sub>2</sub>·9H<sub>2</sub>O (BioXtra,  $\geq 98$  wt%, Sigma-Aldrich), Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (ACS reagent,  $\geq 98$  wt%, Sigma-Aldrich) and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (ACS reagent,  $\geq 98$  wt%, Sigma-Aldrich), with a total cationic concentration of 2 M. The ratios of  $[\text{Mg}^{2+}] : [\text{Al}^{3+}] : [\text{Fe}^{3+}]$  in the precursors for NAFO and NMAFO were 0 : 1 : 1.49 and 1 : 2 : 2.16, respectively. These ratios correspond to mass fractions of Fe<sub>2</sub>O<sub>3</sub> of 71.4% and 54.9%, respectively, in NAFO and NMAFO, if neither oxygen carriers contained Na<sup>+</sup> or any other metal elements. The ratio of  $[\text{Mg}^{2+}] : [\text{Al}^{3+}]$  of 1 : 2 for NMAFO corresponds to the stoichiometric formation of MgAl<sub>2</sub>O<sub>4</sub>, ignoring Fe. The total number of moles of NaOH and Na<sub>2</sub>CO<sub>3</sub> in the alkali solution (the precipitant) was 3 times the total number of moles of metal ions (Mg<sup>2+</sup>, Al<sup>3+</sup> and Fe<sup>3+</sup>) in the nitrate solution (the precursor).

The precipitation was undertaken isothermally at 373 K, at atmospheric pressure. During precipitation, the precursor was added at a constant rate of *ca.* 1 drop per second to a 1 L flask containing the alkali solution, which was stirred constantly at 600 rpm. The temperature of the solution in the flask was held constant at 100 °C, below the point at which the slurry boiled. Loss of water by evaporation was prevented by condensing and refluxing all the vapour at the outlet of the flask. After the addition of the last drop of nitrate solution, the precipitate was kept stirred at 373 K for an additional 24 h. The final pH of the resulting slurry was found to be  $10.0 \pm 0.2$ . Then, the slurry was washed repeatedly with de-ionised water (with an ionic conductivity of  $\sim 20 \mu\text{S cm}^{-1}$ ) until the ionic conductivity of the wash water fell below  $120 \mu\text{S cm}^{-1}$ . Approximately 120 L of de-ionised water was used, over 4 exchanges, to wash each batch of precipitate which yielded 20 g of calcined oxygen carrier. The washed precipitates were filtered, dried at 353 K in air for 24 h, and fired at 1223 K for 3 h. The resulting cake of oxygen carrier was crushed and sieved to a size fraction of 300–425  $\mu\text{m}$  for experiments in a packed bed reactor.

## 2.2. Characterisation of the solids

To characterise the crystalline phases in the solid samples, X-ray powder diffraction (XRD) were performed on a Panalytical X'Pert Pro diffractometer using Cu K $\alpha$  radiation (wavelength = 1.5418 Å), operated at 40 kV and 40 mA. The angle of reflection,  $2\theta$ , was varied between 5 and 60°, at a rate of 0.0167° per step where each step takes 16.5 s. The diffraction patterns were collected at ambient temperature and atmosphere. The collected diffractograms were preliminarily inspected with the aid of reference patterns found in the Inorganic Crystal Structure Database (ICSD). Rietveld refinements were further performed on the collected diffractograms using GSAS with the graphical interface EXPGUI.<sup>16,17</sup> To investigate the elemental composition of the oxygen carriers, loose powders of the oxygen carriers were analysed by an S4 Explorer X-ray fluorescence spectrometer (XRF) system (Bruker AXS GmbH). The surface morphologies of the solid samples were inspected by a scanning

electron microscope (NOVA NANOSEM, FEI), with a secondary electron detector, an accelerating voltage of 5 kV and probe current of 2 nA under high-vacuum ( $6 \times 10^{-5}$  mbar). The samples were sputter-coated with Pt prior to examination by SEM. Energy-dispersive X-ray spectroscopy (EDS) analyses were performed on selected spots on the surface of the solid samples within the same SEM, using an accelerating voltage of 15 kV. The elemental composition at these spots was quantified using the collected EDS spectra and existing calibrations.

The oxygen content available for reduction and oxidation in the oxygen carriers was quantified by reducing the samples isothermally in a thermogravimetric analyser (TGA/DSC1, Mettler Toledo). In a typical TGA experiment, *ca.* 20 mg of fully oxidised sample was placed in a 70  $\mu\text{L}$  alumina crucible, and heated to 1223 K at a rate of 20 K min<sup>-1</sup> under a flow of N<sub>2</sub> (BOC Ltd.) of 50 mL min<sup>-1</sup> (measured at 295 K, 1 atm). After degassing for one hour at 1123 K, an additional flow of 50 mL min<sup>-1</sup> (measured at 295 K, 1 atm) of 5 vol% H<sub>2</sub> in N<sub>2</sub> (Spectrashield, BOC Ltd.) was introduced to the reaction chamber for 10 h before cooling down in N<sub>2</sub> at a rate of  $-20$  K min<sup>-1</sup>. The change in mass of the samples was recorded and the mass fraction of Fe<sub>2</sub>O<sub>3</sub> in the fully oxidised sample was calculated, as shown later in Section 5.1.

To investigate the performance of the oxygen carriers, the samples were cycled under conditions suitable for producing hydrogen by chemical looping in a vertical packed bed. The wall of the tubular reactor (nominal I.D. = 9 mm) was made of recrystallised Al<sub>2</sub>O<sub>3</sub> ( $>99$  wt% purity, Multi-Lab Ltd.). The results of an earlier study by Liu *et al.*<sup>9</sup> confirm that the wall of the tube does not react with Fe-based oxygen carriers under chemical looping conditions, and can be therefore considered as inert. The packing arrangement, from top to bottom, consisted of the following layers of materials: (i) 10.0 g  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (1400–1700  $\mu\text{m}$ ), (ii) approximately 0.3 g of oxygen carrier particles (300–425  $\mu\text{m}$ ), (iii) 2.0 g of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (300–425  $\mu\text{m}$ ), (iv) 2.0 g of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (1400–1700  $\mu\text{m}$ ), and (v) a ceramic distributor plate. The distributor, consisting of three holes of diameter 1.5 mm each in triangular array, was cast using an Al<sub>2</sub>O<sub>3</sub>-based cement (AL/CS – chemical setting adhesive cement, Multi-lab Ltd.) inside the tube. Both ends of the alumina tube were fitted with brass fittings with Viton rubber O-rings acting as seals. The control and gas sampling system for the packed bed has been described elsewhere by Liu *et al.*<sup>9</sup>

During the cycling experiments in the packed bed, the temperature of the active bed was maintained at 1123 K. In each cycle, the gas supplied to the bed consisted successively of: (i) 5 min of reduction by 9.5 vol% CO in N<sub>2</sub> (BOC Ltd.), (ii) 2 min of N<sub>2</sub> purge (Air Liquide UK), (iii) 3 min of oxidation by 12 vol% CO<sub>2</sub> (Air Liquide UK) in N<sub>2</sub> and (iv) 1 min of N<sub>2</sub> purge and (v) 2 min of oxidation by air. Switching between the feed-gases was achieved using solenoid valves. In an additional set of experiments, the freshly-prepared oxygen carriers were cycled without step (v), in order to examine the presence of interaction between Al<sub>2</sub>O<sub>3</sub> and oxides of Fe. Should there be interaction between Al<sub>2</sub>O<sub>3</sub> and oxides of Fe, the absence of step (v) would result in a decay in reactivity and consequently deterioration in the conversion of solid over cycles, as shown by Kidambi *et al.*<sup>7</sup>



It should be noted that  $\text{CO}_2$  was used in step (iii) to simulate the oxidation of reduced iron oxide by steam to produce hydrogen, because the equilibrium values of  $p_{\text{CO}_2}/p_{\text{CO}}$  and  $p_{\text{H}_2\text{O}}/p_{\text{H}_2}$  for the oxidation of Fe to wüstite and wüstite to  $\text{Fe}_3\text{O}_4$  are similar at 1123 K, where  $p_i$  stands for partial pressure of species  $i$ . The validity of using  $\text{CO}_2$  to stimulate steam oxidation for chemical looping hydrogen cycles has also been experimentally confirmed by Liu *et al.*<sup>9</sup> The flowrates of gases at the inlet were controlled and monitored using rotameters or mass flow sensors (Honeywell AWM5103VN). In all stages, the nominal gas flowrates were 1.5 L min<sup>-1</sup> (measured at 295 K, 1 atm). For each sample, the oxygen carrier was cycled 20 times, with or without air-oxidation, *viz.* step (v). The effluent gas from the reactor was analysed by a non-dispersive infrared analyser (NDIR, Uras26, EL3020, ABB), which detects the mole fractions of CO and  $\text{CO}_2$  in the range of 0–10 vol% and 0–12 vol%, respectively.

### 3. Results

#### 3.1. Characterisation of the uncalcined precipitate

X-ray diffraction patterns of the precipitates were collected to investigate the crystalline phases formed during co-precipitation but before calcining at 1223 K; they are shown in Fig. 1. In Fig. 1(a), it can be seen that the dried precipitate consisted of a mixture of  $\text{NaAlCO}_3(\text{OH})_2$  (dawsonite) and  $\text{Fe}_{1.67}\text{H}_{0.99}\text{O}_3$ , a dehydrated form of  $\text{Fe}(\text{OH})_3$ . In Fig. 1(b), the peaks at 11.7° and 23.5° are characteristic of the (0 0 2) and (0 0 4) planes, respectively, of  $\text{Mg}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3 \cdot 3\text{H}_2\text{O}$  (quintinite). The fact that the position of the peaks of the quintinite phase matches closely a reference pattern of pure quintinite ( $\text{Mg}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3 \cdot 3\text{H}_2\text{O}$ , ICSD-182293) suggests that the trivalent sites in the quintinite phase contain little or no  $\text{Fe}^{3+}$ , *i.e.*, almost all  $\text{Fe}^{3+}$  precipitated in the form of  $\text{Fe}(\text{OH})_3$ . Peaks of dawsonite are also seen in Fig. 1(b), together with weak peaks of  $\text{Fe}_{1.67}\text{H}_{0.99}\text{O}_3$ . If there are no amorphous phases present, the

precipitates of (a) NAFO and (b) NMAFO, should contain mixtures of (a) dawsonite and  $\text{Fe}(\text{OH})_3$  and (b) quintinite, dawsonite and  $\text{Fe}(\text{OH})_3$ , respectively. In particular, for NAFO, the composition detected by XRD is also in agreement with the results of XRF shown in Table 1 below. Overall, all peaks in Fig. 1 can be indexed by  $\text{Fe}_{1.67}\text{H}_{0.99}\text{O}_3$ , dawsonite and quintinite.

The precipitates of both samples were also examined by SEM, and the images are shown in Fig. 2. Both images in Fig. 2 show large rod-shaped crystallites, which are characteristic of the dawsonite ( $\text{NaAlCO}_3(\text{OH})_2$ ) phase.<sup>18</sup> In Fig. 2(a), it can be seen that the precipitate also contains spherical agglomerates. Assuming no amorphous phase is present, these spherical agglomerates should be the dehydrated precipitate of  $\text{Fe}(\text{OH})_3$ . Fig. 2(b) shows that the precipitates for NMAFO consist of a mixture of rod-shaped crystals and some small grains. Based on the results of XRD, the latter may be assigned to a mixture of quintinite and  $\text{Fe}(\text{OH})_3$ .

#### 3.2. Characterisation of the calcined precipitate

The mass fraction of the active iron oxide in the calcined precipitates, *i.e.* the freshly-prepared oxygen carriers, was determined by isothermal reduction of the calcined samples in a diluted stream of  $\text{H}_2$  in  $\text{N}_2$  at 1223 K in the TGA. The change in mass of the samples during reduction was rendered dimensionless:

$$\hat{m}_{\text{red}}(t) = m(t)/m(0), \quad (11)$$

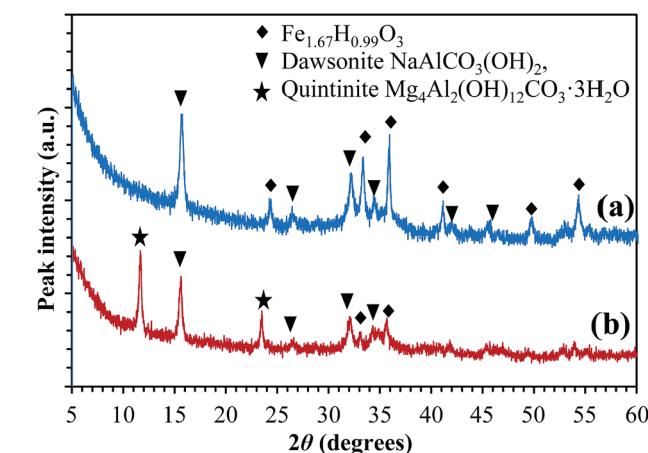
where  $m(0)$  is the mass of the sample just before reduction by  $\text{H}_2$ , at  $t \sim 133$  min, when there was no further weight loss by dehydration and degassing of the solid sample. The resulting profiles of  $\hat{m}_{\text{red}}(t)$  are shown in Fig. 3. Assuming complete reduction of the samples at the end of the experiment,  $x_{\text{Fe}_2\text{O}_3}$ , the mass fraction of  $\text{Fe}_2\text{O}_3$  in the calcined oxygen carrier, was estimated using:

$$x_{\text{Fe}_2\text{O}_3} = [1 - \hat{m}_{\text{red}}(\infty)]/0.301, \quad (12)$$

where  $\hat{m}_{\text{red}}(\infty)$  equals to  $\hat{m}_{\text{red}}$  at the end of the reduction period.

**Table 1** Results of the elemental analysis of the freshly-prepared oxygen carriers by XRF, on oxide basis and metal basis. Contaminants include oxides of Ca, Cr, and Si

XRF analysis, oxide basis (wt%)					
	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{Na}_2\text{O}$	$\text{MgO}$	Contaminants
NAFO	64.3	20.7	12.2	0	2.8
NMAFO	51.7	25.2	10.7	10.2	2.1
XRF analysis, metal basis (mol%)					
	Fe	Al	Na	Mg	Contaminants
NAFO	48.9	24.7	23.9	0	2.5
NMAFO	36.4	27.8	19.4	14.4	2.0



**Fig. 1** X-ray diffraction patterns of the precipitates during the preparation of (a) NAFO and (b) NMAFO, before thermal treatment. All diffraction peaks between 5° and 60° are identified and marked with the corresponding crystalline phases.



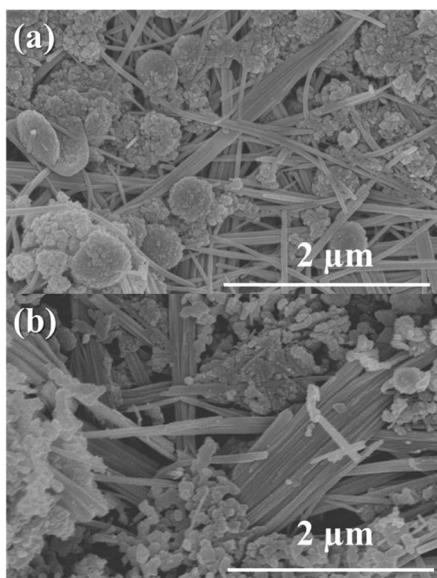


Fig. 2 Scanning electron micrographs of the precipitates during the preparation of (a) NAFO and (b) NMAFO.

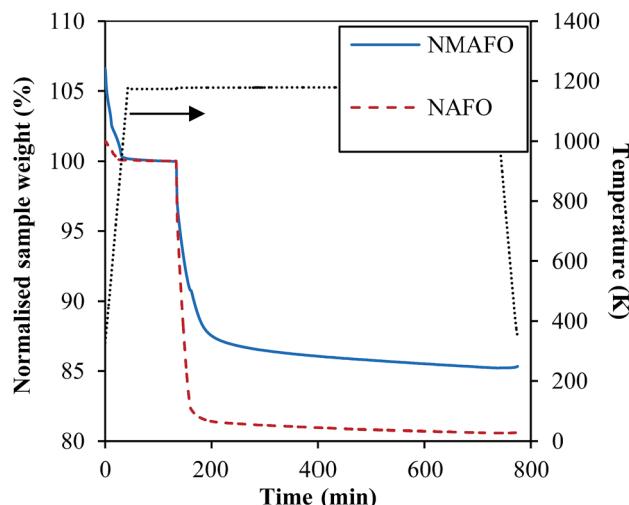


Fig. 3 Normalised sample mass versus time during the isothermal reduction of the freshly-prepared oxygen carriers at 950 °C by  $\text{H}_2$  in  $\text{N}_2$ .

Accordingly,  $x_{\text{Fe}_2\text{O}_3}$  for NAFO and NMAFO were found to be 64.7 and 49.3 wt%, respectively. Both values are lower than those calculated in Section 2.1, assuming the oxygen carriers contain only oxides of  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ . Therefore, the results of the thermogravimetric analysis indicate that both oxygen carriers contain substantial amount of  $\text{Na}^+$ .

The compositions of the crystalline phases of the calcined oxygen carriers were investigated by XRD, the patterns of which are plotted in Fig. 4. In Fig. 4, NAFO was found to contain  $\text{Fe}_2\text{O}_3$  and  $\text{NaAlO}_2$ . For NMAFO, phases of  $\text{Fe}_2\text{O}_3$  (haematite),  $\text{NaAlO}_2$  and  $\text{MgFe}_2\text{O}_4$  were found. Interestingly, the product of the possible interaction between  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$ , *viz.*  $\text{MgAl}_2\text{O}_4$ ,

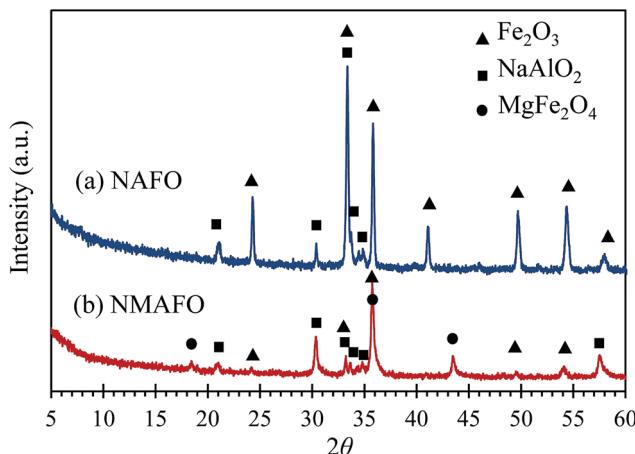


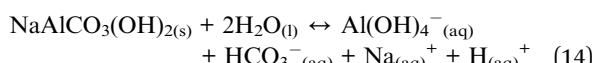
Fig. 4 XRD patterns of the freshly-prepared oxygen carriers of (a) NAFO and (b) NMAFO.

which would generate strong diffraction peaks at *e.g.* 36.9° and 44.9°, was not detected.

In addition to XRD, the elemental composition of the oxygen carriers was quantified by XRF, and results are shown in Table 1. From Table 1, it can be seen that the ratio of [Na] and [Al] is very close to unity in NAFO, indicating that almost all  $\text{Al}^{3+}$  precipitated in the form of  $\text{NaAlCO}_3(\text{OH})_2$ . The ratio of Fe : Al in the freshly-prepared NAFO was found to be ~2, higher than the expected value of 1.49, suggesting some loss of  $\text{Al}^{3+}$  during preparation. This could be a result of  $\text{Al}^{3+}$  in the precipitate re-dissolving under an alkaline environment by:



or



during aging and probably washing. Table 1 also shows that the ratio of [Mg] : [Al] : [Fe] in the freshly-calcined NMAFO is 1 : 1.9 : 2.5, which suggests some loss of  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  during synthesis. However, the ratio of [Mg] : [Al] in NMAFO remains roughly the same as its nitrate precursor, in which [Mg] : [Al] : [Fe] = 1 : 2 : 2.16. Apart from the major metal elements *viz.*  $\text{Na}^+$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  in the case for NMAFO, XRF also detected some contamination by trace elements such as Si, Cr and Ca. The oxides of these contaminants make up less than 2.8% of the total mass of the oxygen carriers. These contaminants probably come from impurities in the chemical precursors. Based on the results of XRF, NAFO and NMAFO contain, respectively, 64.3 and 51.7 wt% of  $\text{Fe}_2\text{O}_3$ , assuming that the metal oxides are fully oxidised and do not form mixed oxides or solid solutions. Here, a solid solution is considered as a single crystal phase, formed from phases with almost identical crystal structure, *e.g.*  $\text{Fe}_3\text{O}_4$  and  $\text{MgFe}_2\text{O}_4$ . The contents of  $\text{Fe}_2\text{O}_3$  deduced by XRF are very close to those estimated from the TGA in Fig. 3, suggesting that all the  $\text{Fe}(\text{m})$  in both oxygen

carriers is eventually reducible in  $H_2$  to  $Fe(0)$ . However, the proportion of  $Fe(III)$  practically reducible to  $Fe(0)$  during chemical looping is discussed in Section 3.3, below.

### 3.3. Cyclic performance in chemical looping

Particles of both oxygen carriers, sized  $d_p = 300\text{--}425\ \mu\text{m}$ , were investigated in a packed bed for the chemical looping production of hydrogen at 1123 K. As mentioned above, the production of hydrogen was simulated by the production of CO by oxidising the reduced oxygen carrier in  $CO_2$ , the redox potential of which is almost identical to that of steam at 1123 K. A total of 20 cycles were performed in each experiment. Profiles of mole fractions of CO and  $CO_2$  in the off-gas during the first two cycles as well as the last cycle in a typical cycling experiment are shown in Fig. 5. Here, the concentration of  $O_2$  during the air-oxidation was not measured. It can be seen from Fig. 5 that, in the case of NMAFO, the profiles were reproducible over the cycles, showing stable performance. The profile of  $CO_2$  produced during reduction, when CO was fed to the inlet, showed an initial sharp rise followed by decay. This is characteristic of the reduction of  $Fe_2O_3$  successively to  $Fe_3O_4$ ,  $FeO$  and  $Fe$ .<sup>19</sup> It should be noted that the concentration of  $CO_2$  did not fall to zero at the end of the reduction, suggesting a conversion of  $Fe_2O_3$  to metallic Fe of less than 100% in each cycle. On the other hand, the rate of oxidation of the reduced carriers by  $CO_2$  fell to zero after 90 s, suggesting fast apparent rates *cf.* reduction. The spike of  $CO_2$  at the very beginning of the oxidation in each cycle was a result of insufficient mixing between  $CO_2$  and  $N_2$  in the feed, immediately after gas-switching, which was achieved using solenoid valves.

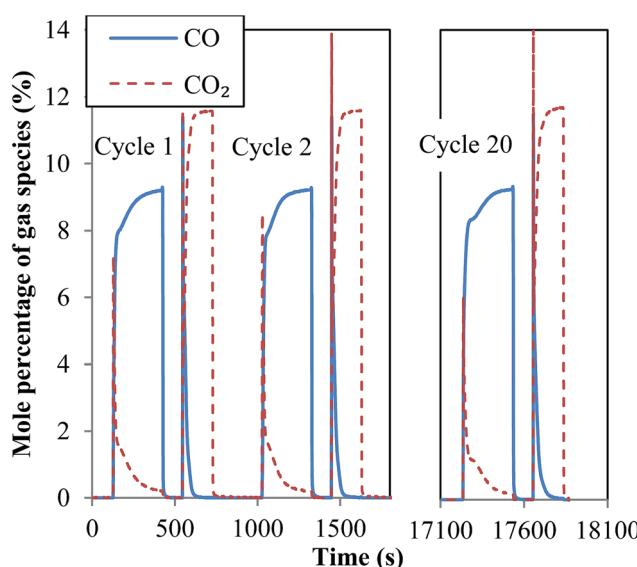


Fig. 5 Variation of the mole fractions of CO and  $CO_2$  in the off-gas of a packed bed, in which a small amount of NMAFO was cycled at 1123 K under conditions equivalent to those suitable for producing hydrogen by chemical looping. The oxygen carrier is tested for 20 cycles, where the profiles of the first two cycles and the last cycle are shown here. The packed bed was oxidised in air at the end of each cycle, although the concentration of oxygen is not measured during the experiments.

The conversion from  $Fe_3O_4$  to Fe,  $X$ , was calculated in two ways, when the oxygen carriers were oxidised in air to  $Fe_2O_3$  at the end of each cycle:

$$X_{\text{red}} = \frac{1}{0.01667} \left( \frac{\dot{N}_{CO+N_2}}{m_0 x_{Fe_2O_3}} \int_0^{300} y_{CO_2} dt - 0.00208 \right) \quad (15)$$

$$X_{\text{ox}} = \frac{1}{0.01667} \frac{\dot{N}_{CO_2+N_2}}{m_0 x_{Fe_2O_3}} \int_{540}^{720} y_{CO} dt \quad (16)$$

here, eqn (15) and (16) calculate  $X$  during the reduction and the subsequent  $CO_2$ -oxidation, respectively. The constants 0.00208 and 0.01667 mol are the stoichiometric amounts of  $CO_2$  produced per g of  $Fe_2O_3$ , for the complete reduction from  $Fe_2O_3$  to  $Fe_3O_4$  and from  $Fe_3O_4$  to Fe, respectively;  $\dot{N}_i$  is the molar flowrate of species  $i$  through the packed bed,  $y_i$  is the measured mole fractions of species  $i$  and  $x_{Fe_2O_3}$  is the mass fraction of  $Fe_2O_3$  (assuming all Fe is in the form of  $Fe_2O_3$ ) in the fully-oxidised sample. Finally,  $m_0$  is the mass in g of the oxygen carrier in its fully-oxidised state and  $t$  is time in s, counting from the first instance when CO was fed to the bed in each cycle. In cases where the bed was not oxidised in air, an alternative expression:

$$X_{\text{red}} = \frac{1}{0.01667} \frac{\dot{N}_{CO+N_2}}{m_0 x_{Fe_2O_3}} \int_0^{300} y_{CO_2} dt \quad (17)$$

was used to calculate  $X_{\text{red}}$ . It should be emphasised that, in this study,  $X$  is a measure of the oxygen carrier's ability to generate hydrogen, *i.e.* the yield of hydrogen in each cycle, if steam is used as an oxidant. A value of  $X$  equal to unity means that all Fe-containing species can be reduced fully to Fe and then oxidised to  $Fe_3O_4$  by steam, giving 100% yield of hydrogen. Eqn (15) also assumes that  $Fe_2O_3$  must be reduced fully to  $Fe_3O_4$  prior to further reduction to  $FeO$  and Fe.

The calculated results of  $X_{\text{red}}$  and  $X_{\text{ox}}$  in each cycle typically differ by less than 1%. Therefore, the arithmetic mean of  $X_{\text{red}}$  and  $X_{\text{ox}}$  was taken as the average value of  $X$  in each cycle. The measured  $X$  were plotted against cycle number in Fig. 6. Fig. 6(a) shows that, when NAF was oxidised by air at the end of each cycle,  $X \sim 100\%$  consistently over 20 cycles. In contrast, without air,  $X$  fell quickly, tending towards 50% by the 20<sup>th</sup> cycle. This diminution is similar to those reported by Bohn *et al.*<sup>5</sup> and Kidambi *et al.*,<sup>7</sup> who studied oxygen carriers made of  $Fe_2O_3$  and  $Al_2O_3$  for chemical looping production of hydrogen and attributed the decaying conversion to the formation of  $FeAl_2O_4$ . Furthermore, Kidambi *et al.*<sup>7</sup> hypothesised two possible reasons for this reduced yield: (i) the presence of the alumina alters the equilibrium for the reduction of iron oxide, making it effectively harder to reduce and (ii) the Fe-Al-O mixture could not prevent sintering over repeated cycles owing to the lack of cyclic phase segregation. In contrast, more consistent performance was seen for NMAFO, as shown in Fig. 6(b), regardless of whether or not air oxidation was used. The measured  $X$ , with and without air, equals to *ca.* 80% over the 20 cycles at 1123 K. These values of  $X$  were less than unity owing to the fact that reduction did not reach completion in each cycle, as discussed above.

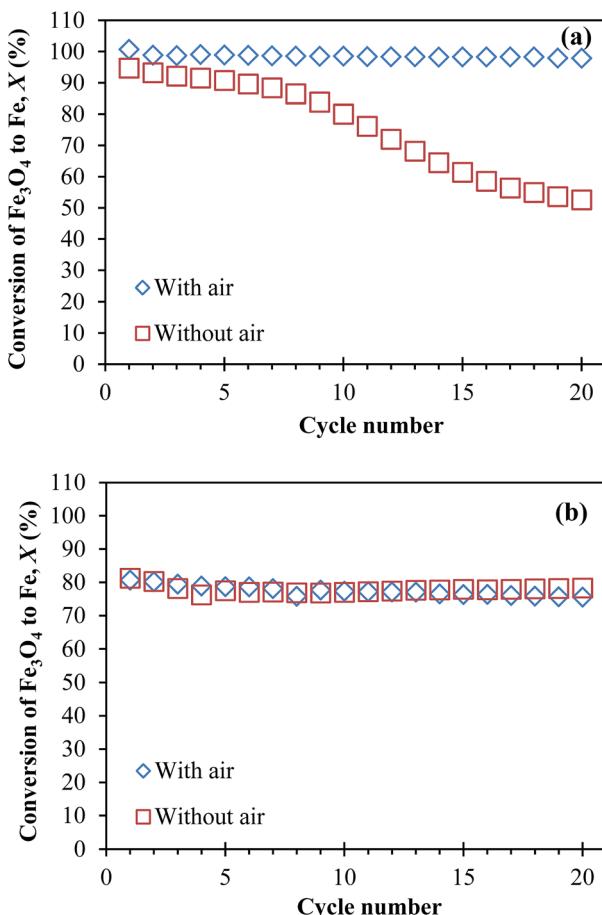


Fig. 6 The conversion of  $\text{Fe}_3\text{O}_4$  to Fe,  $X$  versus cycle number, when approximately 0.3 g of (a) NAFO and (b) NMAFO were cycled in a packed bed reactor in the presence or absence of oxidation by air, at 1123 K. Error bars are too small to be shown here.

Fig. 7 shows the XRD patterns of the oxygen carriers before and after cycling, as well as the fresh samples after various treatments, *viz.* (i) reduction in 10% CO in  $\text{N}_2$  at 1123 K for 10 min and (ii) reduction in a mixture of CO and  $\text{CO}_2$  ( $p_{\text{CO}_2} : p_{\text{CO}} = 1$ ) at 1123 K for 10 min. For NAFO, it can be seen from Fig. 7(a) that, during the reduction of the fresh oxygen carrier, the  $\text{Fe}_2\text{O}_3$  is reduced subsequently to  $\text{Fe}_3\text{O}_4$ ,  $\text{FeO}$  and finally Fe, without any detectable formation of  $\text{FeAl}_2\text{O}_4$ , *i.e.* the interaction between  $\text{FeO}$  and  $\text{Al}_2\text{O}_3$  was absent during the first cycle, and hence the initially high  $X$  seen in Fig. 6(a). However, peaks of  $\text{FeAl}_2\text{O}_4$  can be clearly seen in the sample after 20 cycles without air-oxidation Fig. 7(a)(iv)). This result suggests that there was an accumulation of  $\text{FeAl}_2\text{O}_4$  in NAFO over cycles without air-oxidation. Consequently the reactivity of the oxygen carrier decreases gradually and progressively, as seen in Fig. 6(a). Finally, the two diffraction peaks between 21° and 26° seen in Fig. 7(a)(iv) could not be adequately fitted by Rietveld refinement. With air-oxidation, no  $\text{FeAl}_2\text{O}_4$  is found after cycling, *i.e.*  $\text{FeAl}_2\text{O}_4$  could not accumulate. When fully oxidised in air, the cycled material has a diffraction pattern Fig. 7(a)(v) almost identical to that of the fresh NAFO Fig. 7(a)(i). These XRD patterns suggest that the formation of  $\text{FeAl}_2\text{O}_4$  in NAFO was a

slow and irreversible process in the absence of air-oxidation, but could be reserved by oxidising the oxygen carrier in air at the end of each cycle. In addition, the  $\text{NaAlO}_2$  phase was detected consistently during the reduction and after 20 cycles, indicating it is relatively stable under the conditions used in this study.

The XRD patterns of NMAFO at various stages of the cycling experiment are shown in Fig. 7(b). Here, attention is given to the spinel compounds of  $\text{Fe}_3\text{O}_4$  and  $\text{MgFe}_2\text{O}_4$ , which are mutually soluble and have similar diffraction patterns. For example, the (4 0 0) plane of  $\text{Fe}_3\text{O}_4$  produces a peak at 43.1° whereas for  $\text{MgFe}_2\text{O}_4$  the (4 0 0) peak is at 43.2°. On the other hand, the solid solution of  $\text{MgFe}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  can be easily distinguished from the alumina-based spinel phases of  $\text{FeAl}_2\text{O}_4$  and  $\text{MgAl}_2\text{O}_4$ , the (4 0 0) reflections of which show peaks 44.4° and 44.9°, respectively. The differences between the positions of corresponding peaks are greater at higher angles according to Bragg's Law. Fig. 7(b)(i) shows that the fresh oxygen carrier consists of a mixture of  $\text{Fe}_2\text{O}_3$ ,  $\text{MgFe}_2\text{O}_4$  (possibly with a small amount of  $\text{Fe}_3\text{O}_4$ ) and  $\text{NaAlO}_2$ . Looking at the position of the peaks of  $\text{Fe}_2\text{O}_3$  and  $\text{MgFe}_2\text{O}_4$ , there is no strong evidence to suggest that either phase forms a solid solution with  $\text{Al}_2\text{O}_3$  in the fresh NMAFO. After reduction in an equimolar mixture of  $\text{CO}_2$  and CO (Fig. 7(b)(i)) at 1123 K, the peaks of  $\text{MgFe}_2\text{O}_4$  weaken and those of wüstite start to appear (Fig. 7(b)(ii)). After reduction in CO for 10 min, the crystalline phases detectable are  $\text{MgO}$ , Fe and  $\text{NaAlO}_2$  (Fig. 7(b)(iii)). During the reduction of fresh NMAFO,  $\text{NaAlO}_2$  appeared to be the only crystalline phase that contains Al(III), despite the fact that there is more Al than Na in NMAFO. After 20 cycles at 1123 K without air-oxidation (Fig. 7(b)(iv)), the oxygen carrier is found to contain  $\text{MgFe}_2\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{MgAl}_2\text{O}_4$  and  $\text{NaAlO}_2$ , where the presence of  $\text{Fe}_3\text{O}_4$  is manifested by the peaks of  $\text{MgFe}_2\text{O}_4$  shifting slightly to a lower  $2\theta$  value. With air-oxidation, the XRD pattern of the fully oxidised sample (Fig. 7(b)(v)) shows the same phases as Fig. 7(b)(iv), but with an additional phase of  $\text{Fe}_2\text{O}_3$ . In Fig. 7(b)(v), the positions of peaks of  $\text{Fe}_2\text{O}_3$  and  $\text{MgFe}_2\text{O}_4$  are slightly shifted to the right, suggesting the partial dissolution of  $\text{Al}^{3+}$  in both phases. The dissolution of  $\text{Al}^{3+}$  in  $\text{MgFe}_2\text{O}_4$  is not obvious in Fig. 7(b)(iv), because the effect of shift of peaks of  $\text{MgFe}_2\text{O}_4$  due to  $\text{Al}^{3+}$  might have been cancelled by the opposite effect due to  $\text{Fe}_3\text{O}_4$ . Overall, the evolution of the XRD patterns in Fig. 7(b) shows that, the  $\text{MgFe}_2\text{O}_4$  phase (with some dissolved  $\text{Fe}_3\text{O}_4$ ) was decomposed during reduction, and could be regenerated in  $\text{CO}_2$ . Despite the formation of  $\text{MgFe}_2\text{O}_4$ , the nearly 80%  $X$  seen in Fig. 6(b) demonstrates that this spinel compound did not significantly compromise the reactivity of  $\text{Fe}_2\text{O}_3$ . In addition, the fact that  $\text{MgFe}_2\text{O}_4$  may be regenerated in  $\text{CO}_2$  means there is a potential to produce more hydrogen per mole of Fe by the steam-oxidation of reduced  $\text{MgFe}_2\text{O}_4$  than of pure Fe; this is discussed below in Section 4.2. Lastly, similar to the case of NAFO,  $\text{NaAlO}_2$  was deemed stable under the conditions used for the cycling tests.

Another important aspect indicating the stability of an oxygen carrier is its change in surface morphology with redox cycling. This was investigated by SEM; the results in Fig. 8 show the morphologies of NAFO when (a) fresh, (b) after 20 cycles



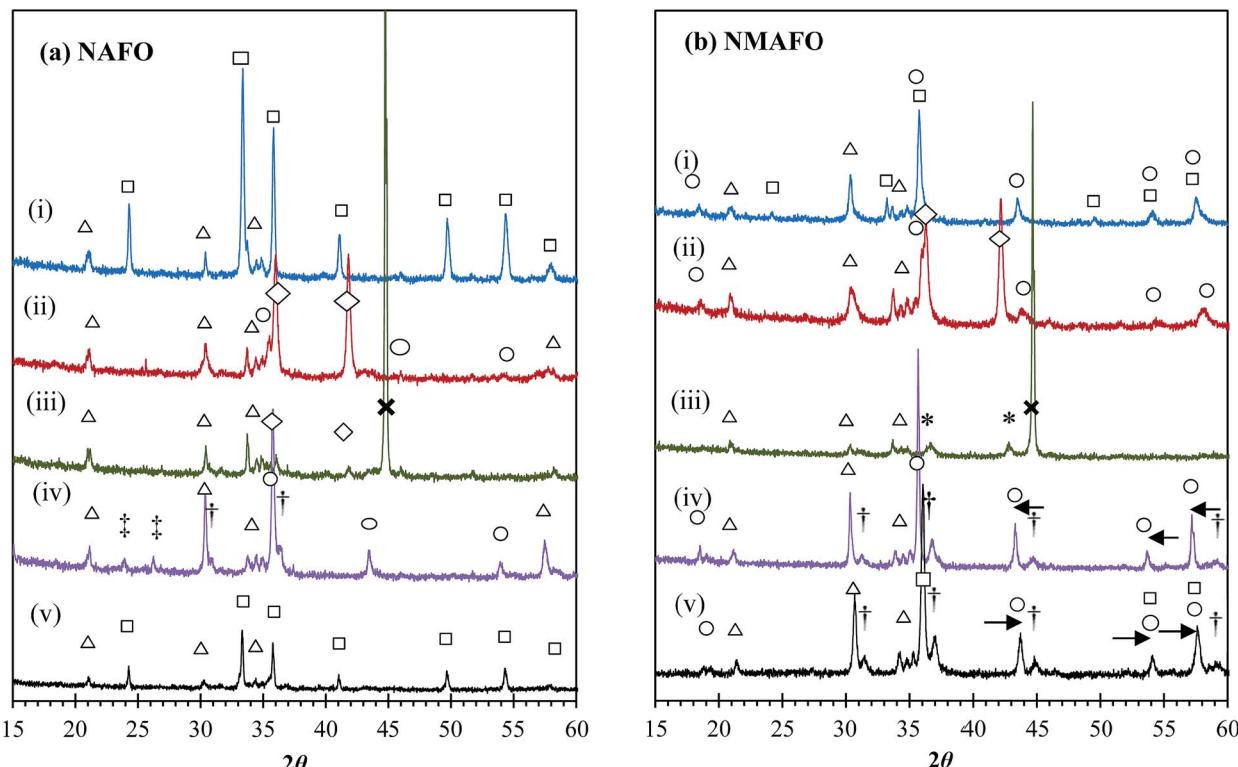


Fig. 7 XRD patterns of (a) NAFO and (b) NMAFO at different stages of the cycling experiments, when they are (i) fresh, (ii) reduced in a mixture of CO and  $\text{CO}_2$  ( $p_{\text{CO}} : p_{\text{CO}_2} = 1$ ) at 1123 K for 10 min, (iii) reduced in 10% CO in  $\text{N}_2$  at 1123 K for 10 min, (iv) oxidised in  $\text{CO}_2$ , after 20 cycles without oxidation in air, and (v) oxidised in air, after 20 cycles with oxidation in air. All peaks are assigned and labelled:  $\triangle$   $\text{NaAlO}_2$ ,  $\square$   $\text{Fe}_2\text{O}_3$ ,  $\circ$  Fe-based spinel (e.g.  $\text{Fe}_3\text{O}_4$  and, or  $\text{MgFe}_2\text{O}_4$ ),  $\diamond$  wüstite,  $*$   $\text{MgO}$ ,  $\times$  Fe, and  $\dagger$  Al-based spinel (e.g.  $\text{MgAl}_2\text{O}_4$  and, or  $\text{FeAl}_2\text{O}_4$ ). The peaks marked by  $\ddagger$  are not indexed. The arrows indicate peak-shifts relative to a pure phase of  $\text{MgFe}_2\text{O}_4$ .

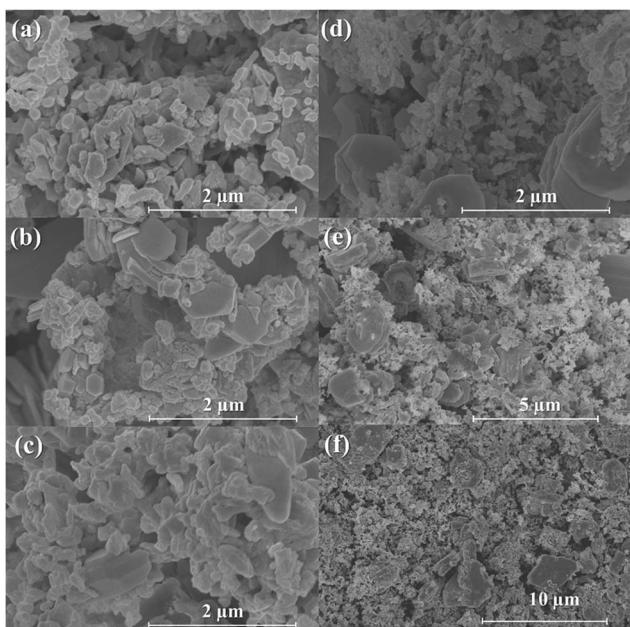


Fig. 8 SEM images of (a) Fresh NAFO; (b) NAFO after 20 cycles without air-oxidation; (c) NAFO after 20 cycles with air-oxidation; (d) fresh NMAFO; and (e) and (f) NMAFO after 20 cycles without air-oxidation at different magnifications.

without air-oxidation and (c) after 20 cycles with air-oxidation, respectively, as well as the surface of particles of NMAFO when (d) fresh and (e) + (f) after 20 cycles without oxidation in air. In all cases, the disappearance of the rod-shaped grains seen in Fig. 2 can be correlated to the decomposition of dawsonite ( $\text{NaAlCO}_3(\text{OH})_2$ ). Fig. 8(a) shows that fresh NAFO, the surface of which is relatively porous, is composed of small, irregularly-shaped grains of uniform size. After 20 cycles without air-oxidation, some large hexagonal crystals were found in NAFO, together with some agglomerated small grains of no particular crystalline feature. When cycled with air-oxidation, the surface of NAFO was found to be mainly composed of uniformly-sized grains similar to those seen in Fig. 8(a). A large grain exhibiting a prismatic crystal habit is also seen in Fig. 8(c); this means that the crystallite has an orthorhombic crystal structure, suggesting that it is made of  $\text{NaAlO}_2$ . On the other hand, both fresh and cycled (without air-oxidation) NMAFO were found to contain large hexagonal crystals of *ca.* 1  $\mu\text{m}$  in size mixed with small grains of *ca.* 100 nm in size. Interestingly, none of the crystalline phases identified in Fig. 7(b)(iv) crystallises hexagonally. To investigate the nature of the hexagonal crystals seen in energy-dispersive X-ray spectra (EDS) of the corresponding samples were taken at points shown in Fig. 9; and the results of the quantitative analysis are presented in Table 2.

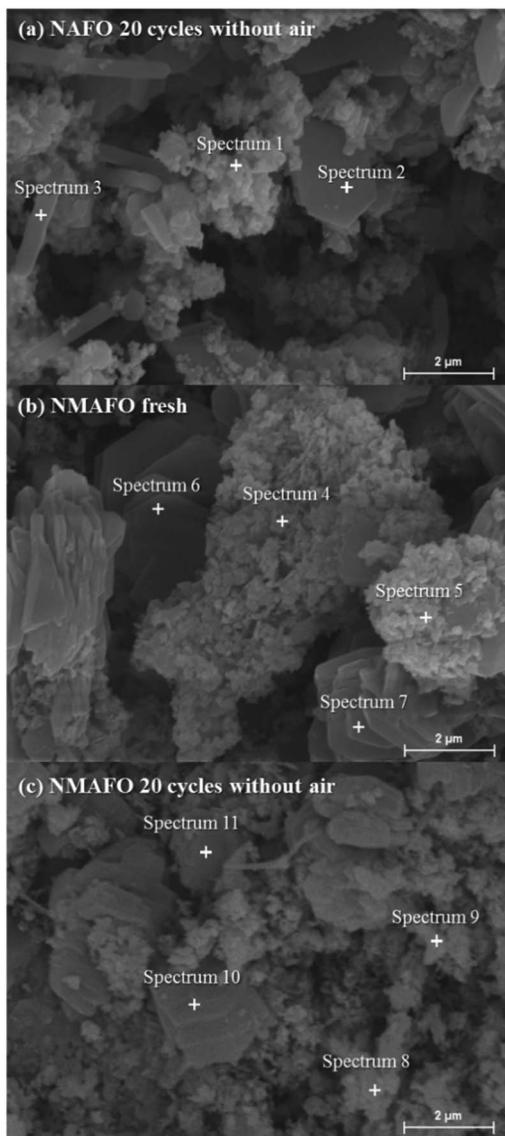


Fig. 9 SEM image of the surface of a particle of (a) NAFO after 20 cycles without oxidation by air, (b) fresh NMAFO and (c) NMAFO after 20 cycles without oxidation by air. Positions where EDS spectra were taken are marked by crosses and results are shown in Table 2.

Table 2 Results of quantitative analysis of EDS spectra taken at points shown in Fig. 9. The compositions of the metal elements are presented in normalised mol%, excluding signals due to C, O and the Pt coating

Spectrum	NAFO 20 cycles without air-oxidation			NMAFO fresh				NMAFO 20 cycles without air-oxidation			
	1	2	3	4	5	6	7	8	9	10	11
Al (mol%)	23	52	21	30	31	87	80	22	38	79	74
Fe (mol%)	63	28	44	26	24	6	10	21	27	15	10
Mg (mol%)	0	0	0	19	19	1	2	20	23	3	9
Na (mol%)	14	21	35	25	26	6	8	38	13	3	6

Here, it should be noted that, the volume of interaction between the electron beam (with an accelerating voltage of 15 kV) and the solid material is several microns wide. Hence, the EDS collected for the hexagonal grains, *e.g.* spectra 2, 10 and 11, might also contain signals produced by the surrounding materials. Therefore, the numbers shown in Table 2 should only be regarded as giving a qualitative indication, which can only be used to estimate the chemical compositions of the hexagonal grains, in combination with other experimental results.

The result of EDS analysis (Fig. 9 and Table 2) suggests that these micron-sized hexagonal grains are predominantly made of  $\text{Al}_2\text{O}_3$ , which means that the “host-phase” of these crystals could be corundum ( $\alpha\text{-Al}_2\text{O}_3$ ),  $\beta$ -alumina ( $(\text{Na}_2\text{O})_n \cdot (\text{Al}_2\text{O}_3)_{11}$ , where  $n = 1\text{--}1.5$ ), or  $\beta''$ -alumina ( $(\text{Na}_2\text{O}) \cdot (\text{Al}_2\text{O}_3)_6$ ). However, the lack of detection of the corundum peaks in Fig. 7 suggests that, the content of  $\text{Al}_2\text{O}_3$  relative to the other phases is low in the bulk of the solid, despite its strong presence at the surface. Furthermore, the strongest peak of  $\text{Al}_2\text{O}_3$  at around  $35^\circ$  could overlap with a peak of  $\text{NaAlO}_2$ , making detection of the former even more difficult. From Fig. 9 and Table 2, it can be also seen that, the metal-based elemental composition of the small, 100 nm-sized grains in NAFO was comparable to the analysis by XRF, although the content of Fe in the small grains in NMAFO appears to be underestimated by EDS.

## 4. Discussion

### 4.1. Performance of NAFO

The experimental results suggest that NAFO underwent several phase changes during its initial preparation and also during the subsequent cycling experiments. The interesting features observed during the experimental investigation of NAFO are discussed in this section.

**4.1.1. Behaviour of NAFO during redox cycling without an air-oxidation step.** Unfortunately, a comprehensive phase diagram for the  $\text{Na-Fe-Al-O}$  system is not available in the literature, so that the following discussion is based on experimental results from both the current study as well those in the existing literature.

Firstly, the chemical inertness of the  $\text{NaAlO}_2$  phase was investigated by XRD for  $27^\circ \leq 2\theta \leq 33^\circ$ , with a slow scanning speed of  $0.00418^\circ$  per 50 s per step. The results of the XRD, shown in Fig. 10, indicate that for both NAFO and NMAFO, the  $(1\ 2\ 0)$  peak of the  $\text{NaAlO}_2$  phase at  $30.3^\circ$  has shifted slightly to a lower  $2\theta$  value after the cycling experiments. Here, the  $\text{NaAlO}_2$  originates from the dawsonite in the original precipitation. This shift could be explained by the dissolution of  $\text{Fe}^{3+}$  into the  $\text{NaAlO}_2$  phase, forming a solid solution with a general formula  $\text{NaAl}_{1-y}\text{Fe}_y\text{O}_2$  ( $0 < y < 1$ ), which is stable even at room temperature.<sup>20</sup> However, Fig. 2(a) suggests, visually, that  $\text{Fe(OH)}_3$  and dawsonite ( $\text{NaAlCO}_3(\text{OH})_2$ ) precipitated heterogeneously during the preparation of NAFO, so that for  $\text{Fe}^{3+}$  – from either  $\text{Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$  – to dissolve in the  $\text{NaAlO}_2$  phase, it would have to migrate a considerable distance to do so. Because the migration of ions in a solid is often a slow process below its melting point, the substitution of  $\text{Al}^{3+}$  by  $\text{Fe}^{3+}$  in  $\text{NaAlO}_2$  might therefore be, kinetically, slow, even though thermodynamically favourable.



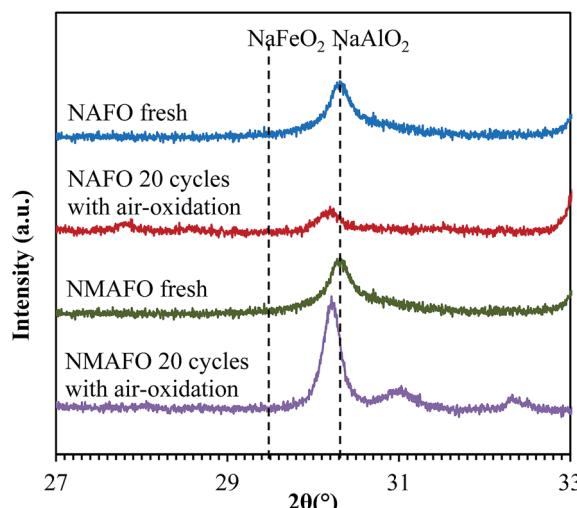


Fig. 10 X-ray diffraction patterns of the oxygen carriers before and after the cycling experiments, when they are fully oxidised in air and cooled to room temperature. Calculated peak positions of the (1 2 0) reflection for both  $\text{NaFeO}_2$  and  $\text{NaAlO}_2$  are marked with dashed lines.

Thus, a plausible explanation to the behaviour of the oxygen carrier is proposed and depicted in Fig. 11. Here, the reaction schematic shown in Fig. 11 postulates that, as a result of the formation of  $\text{NaAl}_{1-y}\text{Fe}_y\text{O}_2$ , where  $y$  increased gradually with time, an increasing amount  $\text{Al}^{3+}$  was displaced from the  $\text{NaAl}_{1-y}\text{Fe}_y\text{O}_2$  phase, and became free to interact with oxides of Fe. Evidence for this explanation comes from XRD measurements on fresh carrier and carrier cycled many times. Initially, the freshly-calcined oxygen carrier contained a mixture of  $\text{NaAlO}_2$  and  $\text{Fe}_2\text{O}_3$ , both of which were detected by XRD, as seen in Fig. 7(a)(i). In the first cycle, the only reactive species in the fresh NAFO was  $\text{Fe}_2\text{O}_3$ , whilst the  $\text{NaAlO}_2$  was more or less stable, as seen in Fig. 7(a)(i)–(iii). In other words, almost all the  $\text{Fe}^{3+}$  in NAFO was present as  $\text{Fe}_2\text{O}_3$ , which could be reduced

completely to Fe, resulting in the observed  $X$  of  $\sim 100\%$ . However, peaks of  $\text{FeAl}_2\text{O}_4$  can be clearly seen in the sample after 20 cycles without air-oxidation (Fig. 7(a) (iv)), suggesting that a substantial amount of  $\text{Al}^{3+}$  was made available to interact with  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{FeO}$ . In particular, the formation of  $\text{FeAl}_2\text{O}_4$  has been known to be responsible for the decaying performance of the Fe-based oxygen carriers in the absence of an air-oxidation step.<sup>6,7</sup> Thus far, the theory matches the experimental facts.

**4.1.2. Behaviour of NAFO during redox cycling with an air-oxidation step.** This section considers the picture when there is air oxidation included in each cycle and how the mechanism just posited is altered; this is also depicted in Fig. 11. Firstly, despite an increasing value of  $y$  in the  $\text{NaAl}_{1-y}\text{Fe}_y\text{O}_2$  phase, the consistently high conversion over the 20 cycles with air-oxidation shown in Fig. 6(a) means that, the accumulation of  $\text{Fe}^{3+}$  in  $\text{NaAl}_{1-y}\text{Fe}_y\text{O}_2$  by itself was not deleterious to the reactivity of the oxygen carrier, and that the  $\text{Fe}^{3+}$  in  $\text{NaAl}_{1-y}\text{Fe}_y\text{O}_2$  could be fully reduced and oxidised in each cycle. Here, it should be remembered that the  $\text{Fe}^{3+}$  in the  $\text{NaAl}_{1-y}\text{Fe}_y\text{O}_2$  phase is stable in  $\text{CO}_2$  or  $\text{H}_2\text{O}$  and cannot be oxidised further. Secondly, Bohn *et al.*<sup>5</sup> and Kidambi *et al.*<sup>7</sup> showed that the decay in performance of the  $\text{Fe}_2\text{O}_3\text{--Al}_2\text{O}_3$  based oxygen carriers can be minimised by oxidation in air at the end of every cycle, an observation reinforced by the results in Fig. 6(a). Kidambi *et al.*<sup>7</sup> showed further that the unreactive spinel,  $\text{FeAl}_2\text{O}_4$ , formed by the interaction within the Fe–Al–O system, could be eliminated by oxidation with air because, with such treatment, any  $\text{FeAl}_2\text{O}_4$  formed decomposed to alumina and haematite, and simple solid solutions thereof, in line in fact with the thermodynamic predictions from the Fe–Al–O phase diagram. Accordingly, it is concluded that (i) the addition of  $\text{Na}_2\text{O}$  alone to a mixture of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  is insufficient to prevent the Fe–Al–O interaction, and (ii) the accumulation of the resulting  $\text{FeAl}_2\text{O}_4$  spinel will lead to a progressive reduction in reactivity unless it is decomposed by air-oxidation in each cycle.

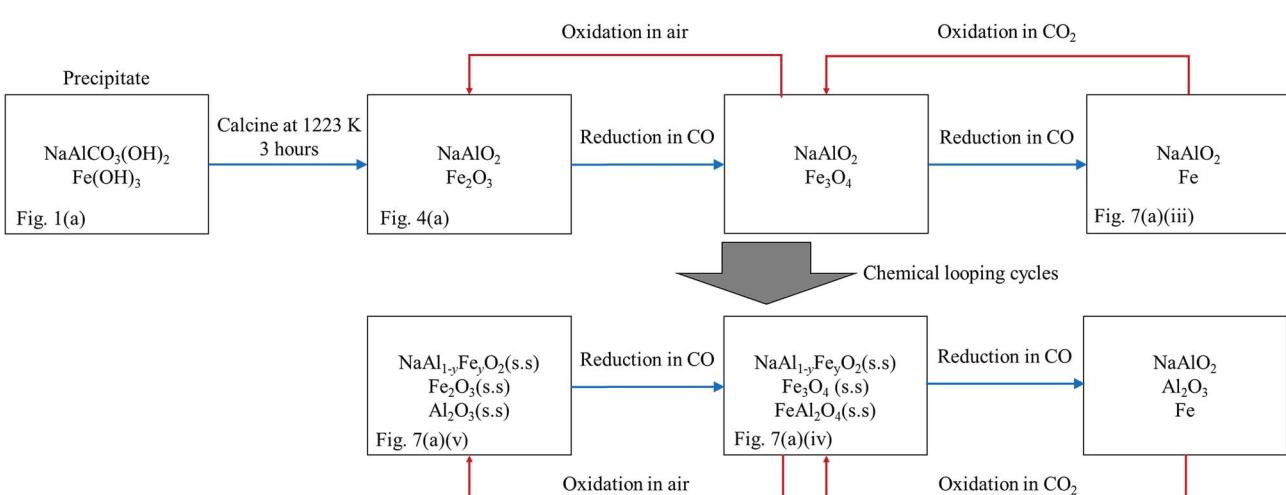


Fig. 11 A schematic diagram showing the change of composition of the oxygen carrier NAFO at various stages of the experimental investigation. The availability of the corresponding XRD patterns is denoted at the bottom of the boxes.



#### 4.2. Performance of NMAFO

Here, the changes in composition during the preparation and investigation of NMAFO are depicted in Fig. 12 and discussed below. In NMAFO, MgO has been added to the oxygen carrier such that  $[Mg] : [Al] = 0.5$ , a ratio theoretically sufficient to bind all the  $Al_2O_3$  in the form of  $MgAl_2O_4$ , even if no sodium aluminate phase forms. The results of XRF, shown in Table 1, indicate that in NMAFO the ratio  $[Al] : [Na] \gg 1$ . Therefore, besides  $NaAlO_2$ , there should be at least one more Al-containing phase present in the freshly-calcined oxygen carrier. The results of EDS analysis, shown in Fig. 9 and Table 2, suggest that this Al-containing phase could be  $Al_2O_3$  (corundum), which appears to be stable in the form of large hexagonal crystals before and after the cycling experiments, with or without air-oxidation. In addition, the absence of  $MgAl_2O_4$  peaks in Fig. 7(b)(i)–(iii), and the absence of cubic crystals in Fig. 8(d), suggest that the fresh NMAFO contains very little  $MgAl_2O_4$ .

As with NAFO,  $NaAl_{1-y}Fe_yO_2$  was progressively formed with cycling and its presence verified by XRD, with evidence shown in Fig. 10. Therefore, analogous to the case for NAFO, it is suggested here that the initially pure  $NaAlO_2$  phase is gradually doped with  $Fe^{3+}$ , progressively forming  $NaAl_{1-y}Fe_yO_2$  over the course of the cycling experiments. Then, the displaced  $Al^{3+}$  ions are simultaneously absorbed by:  $MgFe_2O_4 + Al_2O_3 = MgAl_2O_4 + Fe_2O_3$ . Consequently,  $MgAl_2O_4$  accumulated over time, and is clearly seen in Fig. 7(b) (iv) and (v). In the extreme scenario where all the  $Al^{3+}$  ions are eventually displaced by  $Fe^{3+}$  in the  $NaAl_{1-y}Fe_yO_2$  phase, a ratio of  $[Mg] : [Al] = 0.5$  would ensure that  $FeAl_2O_4$  does not form. Hence, the oxygen carrier showed consistent conversion from  $Fe_3O_4$  to Fe of  $\sim 80\%$  with or without air-oxidation over 20 cycles at 1123 K. In passing, it should be also noted that the conversion is less than unity in Fig. 6(b) because the reduction was not completed in each cycle, as indicated by the non-zero  $[CO_2]$  at the end of each reduction step in Fig. 5.

Prior to the formation of  $MgAl_2O_4$ , all the MgO is assumed to be present in the form of  $MgFe_2O_4$ , as shown in Fig. 12. Thus,

the reactive phases in the freshly-calcined NMAFO should be, by simple stoichiometry, a mixture of 51.0 wt%  $MgFe_2O_4$  and 13.9 wt%  $Fe_2O_3$ , with a ratio of  $[Fe]/([Fe] + [Mg]) \sim 0.73$ , together with  $NaAlO_2$ , which remains effectively stable during the first cycle. After cycling, the XRD patterns in Fig. 7(b)(iv) and (v) suggest that there remains substantial amounts of  $MgFe_2O_4$ . In contrast with  $FeAl_2O_4$ , the spinel  $MgFe_2O_4$  formed in NMAFO appeared to be readily reducible under the conditions of experimentation used and so its formation did not lead to a fall in the reactivity of NMAFO.

The phase diagram of the Mg–Fe–O system at 1123 K, calculated using MTDATA<sup>21</sup> and plotted in Fig. 13, can be used to explore the thermodynamics further. Fig. 13 shows that, in the Mg–Fe–O system, the reduction of NMAFO, in which  $Fe/(Fe + Mg) \sim 0.73$  in

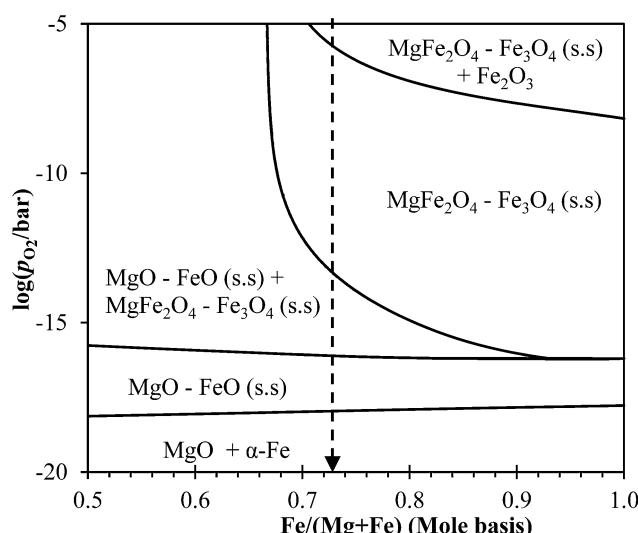


Fig. 13 Calculated phase diagram of the Mg–Fe–O showing  $\log(p_{O_2}/\text{bar})$  versus cationic mole fraction of Fe at 1123 K, at the Fe-rich side. The dashed line marks the molar ratio of  $Fe : (Fe + Mg) \sim 0.73$  in NMAFO.

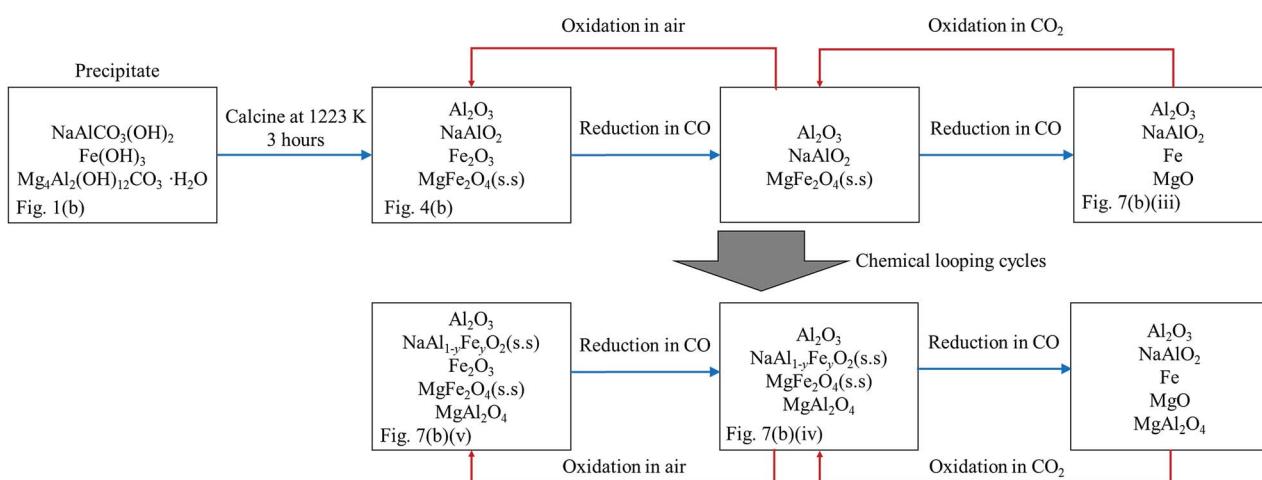


Fig. 12 A schematic diagram showing the change of composition of the oxygen carrier NMAFO at various stages of the experimental investigation. The availability of the corresponding XRD patterns is denoted at the bottom of the boxes.

$+ \text{Mg} > 0.68$ , involves three phase transitions: (i) haematite to  $\text{MgFe}_2\text{O}_4\text{--Fe}_3\text{O}_4$  solid solution, (ii)  $\text{MgFe}_2\text{O}_4\text{--Fe}_3\text{O}_4$  solid solution to  $\text{MgO}\text{--FeO}$  solid solution, and (iii)  $\text{MgO}\text{--FeO}$  solid solution to metallic Fe. These three phase transitions are analogous to the three phases in the reduction of  $\text{Fe}_2\text{O}_3$  sequentially to  $\text{Fe}_3\text{O}_4$ , FeO and Fe. However, in the presence of  $\text{Mg}^{2+}$ , the phase transitions from haematite to spinel ( $\text{Fe}_3\text{O}_4$  and  $\text{MgFe}_2\text{O}_4$ ) and then to halite ( $\text{MgO}$  and  $\text{FeO}$ ) occur at higher values of equilibrium  $p_{\text{O}_2}$  than for the corresponding transitions with pure iron oxides. Thus, thermodynamically, the  $\text{MgO}\text{--Fe}_2\text{O}_3$  mixture could in fact be more readily reducible than pure  $\text{Fe}_2\text{O}_3$ . On the other hand, in a commercial chemical looping process, where the reduced oxygen carrier is oxidised by steam, the hydrogen produced by the reduced NMAFO would be more dilute than that by pure Fe, because of the shifted-equilibrium; this is a potential drawback because more steam is needed for each mole of hydrogen produced using NMAFO. Another implication of the Mg–Fe–O phase diagram is that, in NMAFO, a larger proportion of Fe could be oxidised to  $\text{Fe}(\text{III})$  by steam than for pure  $\text{Fe}_2\text{O}_3$ . However, taking into account the dilution by  $\text{MgO}$ , the theoretical yield of hydrogen per unit mass of fully-oxidised oxygen carrier, for any  $\text{MgFe}_2\text{O}_4\text{--Fe}_2\text{O}_3$  mixture, is still lower than that for unmodified  $\text{Fe}_2\text{O}_3$ . To investigate the assertions mentioned above, the behaviour of a mixed oxide containing only Mg and Fe, *e.g.*  $\text{MgFe}_2\text{O}_4$ , should be studied in future work. Interestingly, a molar ratio of  $\text{Mg} : \text{Fe} : \text{Al} = 3.5 : 6 : 1$  could be fruitful in future investigations, because such a composition corresponds to an oxygen carrier consisting of  $\text{MgFe}_2\text{O}_4$  (as an active component) and  $\text{MgAl}_2\text{O}_4$  (as a support). Thus, the use of  $\text{Mg}^{2+}$  as an inhibitor as well as a promoter might be optimised.

Finally, Fig. 13 shows that, during the cycling experiments, the  $\text{MgFe}_2\text{O}_4\text{--Fe}_2\text{O}_3$  mixture in NMAFO would be transformed between single-phase regions and two-phase mixtures repeatedly. It is believed that cycling between a two-phase mixture and a single-phase solid solution could give oxygen carriers a regenerable porous structure, which renders superior cyclic stability over conventional oxygen carriers, *e.g.* metal oxides mixed with catalyst supports.<sup>7,22</sup> Dunstan *et al.*<sup>22</sup> have suggested that a similar mechanism might explain the longevity of their high-temperature sorbents for the capture and release of  $\text{CO}_2$ , where the solid sorbents undergo changes in molar volume cyclically at a temperature similar to that used in this study. Nevertheless, it must be remembered that, in practice, the oxygen carrier would have to withstand several thousand of cycles of reduction and oxidation. Therefore, other properties, such as resistance against fracture due to repeated change in molar volume and resistance against attrition, must be considered for the future development of the oxygen carrier.

In conclusion, the oxygen carrier NMAFO worked well, probably because (i) the interaction involving Fe–Al–O was prevented by the formation of  $\text{MgAl}_2\text{O}_4$  and (ii) the thermodynamic properties of the Mg–Fe–O system were utilised, in which the formation of spinel phase and various solid solutions might have improved the “reducibility” of the Fe-based oxygen carriers. This contrasts with the decaying reactivity seen in the Fe–Al–O system.

In the light of the above results, it would also be interesting to investigate the potential use of other elements in group II, *e.g.* Ca and Sr, as well as other divalent metal oxides, to stabilise a mixture of Fe–Al–O and to promote the reactivity of oxides of Fe in the chemical looping production of hydrogen. In fact, analogous systems, *viz.* Ni–Fe–O and Co–Fe–O have been studied by Aston *et al.*<sup>23</sup> for the production of hydrogen by chemical looping. Accordingly, Aston *et al.*<sup>23</sup> found that both  $\text{NiFe}_2\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  could be reduced to  $\text{FeO}$  at higher  $p_{\text{CO}_2}/p_{\text{CO}}$  than pure  $\text{Fe}_2\text{O}_3$ , but at the cost of a higher equilibrium value of  $p_{\text{H}_2\text{O}}/p_{\text{H}_2}$  during the generation of  $\text{H}_2$ . All of these mixed oxide systems have demonstrated the potential of altering the thermodynamics of conventional oxygen carriers by using mixed oxides for chemical looping, a technique which can be engineered to suit a wide range of chemical processes involving redox reactions.

## 5. Conclusion

Fe-based oxygen carriers, consisting of oxides of (i) Na, Al and Fe (NAFO) and (ii) Na, Mg, Al and Fe (NMAFO) were synthesised by means of co-precipitation using a technique involving a gradual reduction in the pH of the solution containing the precursor salts. The major components in the precipitates were  $\text{Fe}(\text{OH})_3$ ,  $\text{NaAlCO}_3(\text{OH})_2$  (dawsonite), and in the case of NMAFO,  $\text{Mg}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3 \cdot 3\text{H}_2\text{O}$  (quintinite); the corresponding oxygen carriers were obtained by calcining these precipitates. Such formulations could in theory prevent the formation of  $\text{FeAl}_2\text{O}_4$ , by forming instead the thermodynamically more stable  $\text{MgAl}_2\text{O}_4$  and  $\text{NaAlO}_2$ , which could also act as support materials to stabilise the reactivity of the active  $\text{Fe}_2\text{O}_3$ . The spinel  $\text{FeAl}_2\text{O}_4$  leads to a progressive diminution in the yield of hydrogen unless the carrier is fully oxidised on each cycle using air. It was found that, the sodium in NAFO was unable to prevent the interaction between  $\text{Al}_2\text{O}_3$  and iron oxide, whereas in NMAFO, the excess  $\text{MgO}$  used assisted in inhibiting the interaction. When cycled under conditions suitable for producing hydrogen at 1123 K, both oxygen carriers showed stable performance over 20 cycles, demonstrating  $\sim 100\%$  and  $\sim 80\%$ , respectively, of their theoretical capacities to produce hydrogen, when they were oxidised in air at the end of each cycle. However, without air-oxidation, the performance of NAFO was found to decay with cycling, attributed to the gradual, progressive formation of  $\text{FeAl}_2\text{O}_4$ . In contrast, the performance of NMAFO was found to be stable and consistent with cycling regardless of the inclusion of air-oxidation. The experiments suggested that, although there was some evidence that  $\text{NaAlO}_2$  resisted the formation of  $\text{FeAl}_2\text{O}_4$ , this resistance was slowly compromised by the gradual replacement of  $\text{Al}^{3+}$  by  $\text{Fe}^{3+}$  in  $\text{NaAlO}_2$ , leading to the formation of “free”  $\text{Al}_2\text{O}_3$ . This alumina reacted with  $\text{FeO}$  to form the unreactive  $\text{FeAl}_2\text{O}_4$  in NAFO. However, in NMAFO, free alumina was postulated to react preferentially with  $\text{Mg}^{2+}$  to form  $\text{MgAl}_2\text{O}_4$  instead of  $\text{FeAl}_2\text{O}_4$  spinel. The unique thermodynamic properties of the Mg–Fe–O system might also be responsible for the outstanding performance of the NMAFO oxygen carrier.

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## Notes and references

- 1 B. C. H. Steele and A. Heinzel, *Nature*, 2001, **414**, 345–352.
- 2 C. D. Bohn, C. R. Müller, J. P. Cleeton, A. N. Hayhurst, J. F. Davidson, S. A. Scott and J. S. Dennis, *Ind. Eng. Chem. Res.*, 2008, **47**, 7623–7630.
- 3 A. Messerschmitt, *US Pat.*, 971,216, 1910.
- 4 H. Reed and H. Berg, *US Pat.* 2,635,947, 1953.
- 5 C. D. Bohn, J. P. Cleeton, C. R. Müller, S. Y. Chuang, S. A. Scott and J. S. Dennis, *Energy Fuels*, 2010, **24**, 4025–4033.
- 6 A. M. Kierzkowska, C. D. Bohn, S. A. Scott, J. P. Cleeton, J. S. Dennis and C. R. Müller, *Ind. Eng. Chem. Res.*, 2010, **49**, 5383–5391.
- 7 P. R. Kidambi, J. P. E. Cleeton, S. A. Scott, J. S. Dennis and C. D. Bohn, *Energy Fuels*, 2012, **26**, 603–617.
- 8 J. P. E. Cleeton, Ph.D. thesis, University of Cambridge, 2011.
- 9 W. Liu, J. S. Dennis and S. A. Scott, *Ind. Eng. Chem. Res.*, 2012, **51**, 16597–16609.
- 10 P. Gayán, L. F. de Diego, F. García-Labiano, J. Adánez, A. Abad and C. Dueso, *Fuel*, 2008, **87**, 2641–2650.
- 11 H. Jin, T. Okamoto and M. Ishida, *Ind. Eng. Chem. Res.*, 1999, **38**, 126–132.
- 12 T. Mattisson, M. Johansson and A. Lyngfelt, *Energy Fuels*, 2004, **18**, 628–637.
- 13 Q. Imtiaz, A. M. Kierzkowska, M. Broda and C. R. Müller, *Environ. Sci. Technol.*, 2012, **46**, 3561–3566.
- 14 Q. Imtiaz, A. M. Kierzkowska and C. R. Müller, *ChemSusChem*, 2012, **5**, 1610–1618.
- 15 Q. Song, W. Liu, C. D. Bohn, R. N. Harper, E. Sivanah, S. A. Scott and J. S. Dennis, *Energy Environ. Sci.*, 2012, **6**, 288–298.
- 16 A. C. Larson and R. B. Von Dreele, *General Structure Analysis System (GSAS)*, Los Alamos national Laboratory Report, LAUR, 2000, pp. 86–748.
- 17 B. H. Toby, *J. Appl. Crystallogr.*, 2001, **34**, 210–213.
- 18 H. Hellevang, J. Declercq, B. Kvamme and P. Aagaard, *Appl. Geochem.*, 2010, **25**, 1575–1586.
- 19 W. Liu, J. Y. Lim, M. A. Saucedo, A. N. Hayhurst, S. A. Scott and J. S. Dennis, *Chem. Eng. Sci.*, 2014, **120**, 149–166.
- 20 R. Davies, A. Dinsdale, J. Gisby, J. Robinson and S. Martin, *Calphad*, 2002, **26**, 229–271.
- 21 J. J. Bara, B. F. Bogacz, T. Jaworska, J. Leciejewicz, M. Styczyńska and A. Szytuła, *J. Magn. Magn. Mater.*, 1988, **75**, 73–78.
- 22 M. T. Dunstan, W. Liu, A. F. Pavan, J. A. Kimpton, C. D. Ling, S. A. Scott, J. S. Dennis and C. P. Grey, *Chem. Mater.*, 2013, **25**, 4881–4891.
- 23 V. J. Aston, B. W. Evanko and A. W. Weimer, *Int. J. Hydrogen Energy*, 2013, **38**, 9085–9096.

