

Cite this: *J. Mater. Chem. A*, 2022, 10, 10692

# Na- $\beta$ -Al<sub>2</sub>O<sub>3</sub> stabilized Fe<sub>2</sub>O<sub>3</sub> oxygen carriers for chemical looping water splitting: correlating structure with redox stability†

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Chemical looping is an emerging technology to produce high purity hydrogen from fossil fuels or biomass with the simultaneous capture of the CO<sub>2</sub> produced at the distributed scale. This process requires the availability of stable Fe<sub>2</sub>O<sub>3</sub>-based oxygen carriers. Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> based oxygen carriers exhibit a decay in the H<sub>2</sub> yield with cycle number, due to the formation of FeAl<sub>2</sub>O<sub>4</sub> that possesses a very low capacity for water splitting at typical operating conditions of conventional chemical looping schemes (700–1000 °C). In this study, the addition of sodium (*via* a sodium salt) in the synthesis of Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> oxygen carriers was assessed as a means to counteract the cyclic deactivation of the oxygen carrier. Detailed insight into the oxygen carrier's structure was gained by combined X-ray powder diffraction (XRD), X-ray absorption spectroscopy (XAS) at the Al, Na and Fe K-edges and scanning transmission electron microscopy/energy-dispersive X-ray spectroscopy (STEM/EDX) analyses. The addition of sodium prevented the formation of FeAl<sub>2</sub>O<sub>4</sub> and stabilized the oxygen carrier *via* the formation of a layered structure, Na- $\beta$ -Al<sub>2</sub>O<sub>3</sub> phase. The material, *i.e.* Na- $\beta$ -Al<sub>2</sub>O<sub>3</sub> stabilized Fe<sub>2</sub>O<sub>3</sub>, showed a stable H<sub>2</sub> yield of ca. 13.3 mmol g<sup>-1</sup> over 15 cycles.

Received 8th December 2021  
Accepted 11th April 2022

DOI: 10.1039/d1ta10507h

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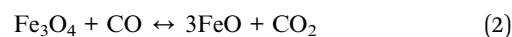
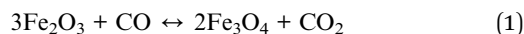
## Introduction

Hydrogen is an emerging energy carrier with potential applications in the transport, industry and power sectors as a fuel that yields water vapour as the only combustion product. If produced sustainably, H<sub>2</sub> has the potential to become a near-zero emissions energy carrier, hence reducing energy-related CO<sub>2</sub> emissions.<sup>1–3</sup> Currently, the majority of H<sub>2</sub> is produced from natural gas *via* steam methane reforming (SMR) without carbon dioxide capture, which is an energy intensive process and emits a significant amount of CO<sub>2</sub>.<sup>3,4</sup> In addition, further energy-intensive purification steps are required to obtain H<sub>2</sub> of sufficiently high purity allowing its use in polymer electrolyte membrane fuel cells (PEMFC).<sup>5,6</sup> Hence, for H<sub>2</sub> to become an energy carrier in a sustainable framework, it must be produced in an efficient and sustainable manner, *i.e.* from renewable sources or with CO<sub>2</sub> capture.<sup>7,8</sup>

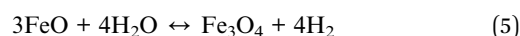
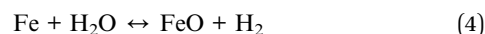
A chemical looping (CL) scheme based on the cyclic redox reactions of iron oxide/iron offers the possibility to produce high purity H<sub>2</sub> with inherent CO<sub>2</sub> capture (Fig. 1a).<sup>7–14</sup> This process could be operated using different reducing gases such

as CO, synthesis gas (produced by biomass gasification) or natural gas.<sup>15,16</sup> For instance, CO is used to reduce Fe<sub>2</sub>O<sub>3</sub> to lower oxidation states (ideally to metallic Fe which gives the highest H<sub>2</sub> yield), following reactions (1)–(3). During Fe<sub>2</sub>O<sub>3</sub> reduction, a pure stream of CO<sub>2</sub> is obtained readily through the condensation of water vapour. The oxidation of metallic Fe with steam produces H<sub>2</sub> (water splitting reactions (4) and (5)) of high purity.<sup>17</sup> To close the cycle, Fe<sub>3</sub>O<sub>4</sub> is oxidized to Fe<sub>2</sub>O<sub>3</sub> in air (reaction (6)).

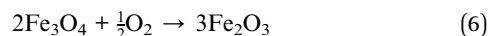
Reduction of iron oxide in CO



Oxidation in steam



Oxidation in air



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† Electronic supplementary information (ESI) available. See <https://doi.org/10.1039/d1ta10507h>



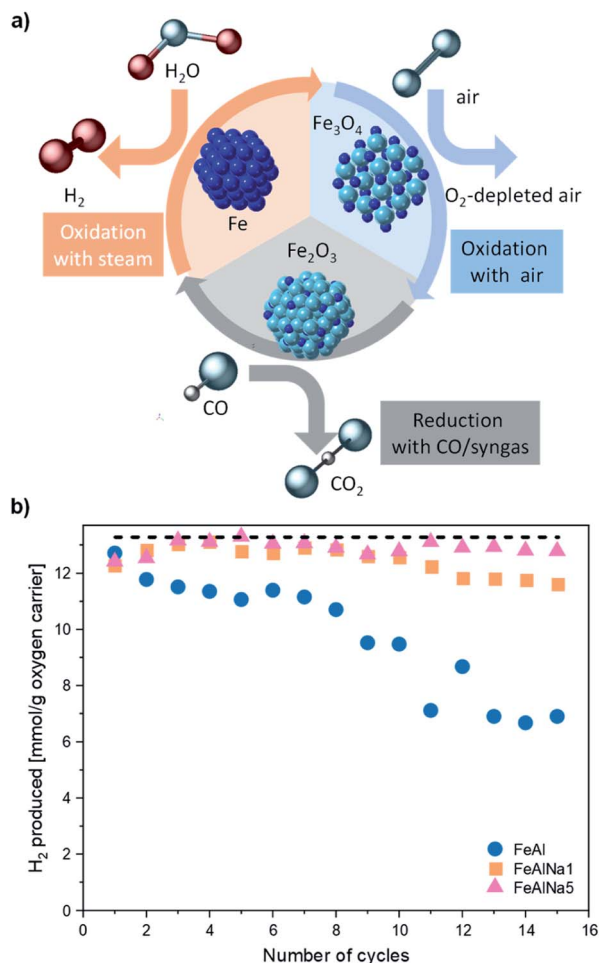


Fig. 1 (a) Schematic of the Fe<sub>2</sub>O<sub>3</sub>-Fe based chemical looping process for the production of H<sub>2</sub> using a synthesis gas (H<sub>2</sub> and CO) as the fuel. (b) H<sub>2</sub> yield as a function of cycle number for FeAl, FeAlNa1 and FeAlNa5. The redox experiments were performed at 800 °C in a packed-bed reactor using 10 vol% CO in N<sub>2</sub> for reduction and 23 vol% H<sub>2</sub>O in N<sub>2</sub> followed by 5 vol% O<sub>2</sub> in N<sub>2</sub> for re-oxidation. The dashed horizontal line represents the theoretically expected H<sub>2</sub> yield (13.3 mmol g<sup>-1</sup>) for an oxygen carrier that contains 80 wt% Fe<sub>2</sub>O<sub>3</sub>.

Owing to its favourable thermodynamics iron oxide is one of the most attractive oxygen carriers for the chemical-looping based production of hydrogen.<sup>7–11,13,17–27</sup> However, pure Fe<sub>2</sub>O<sub>3</sub> shows a rapid decay in its H<sub>2</sub> yield with number of redox cycles owing to sintering.<sup>17</sup> Sintering leads to an appreciable decrease in the reduction rate of iron oxide, which results in an incomplete reduction and in turn a low H<sub>2</sub> yield in the subsequent re-oxidation step.<sup>7,27,28</sup> To mitigate deactivation by sintering, strategies based on the addition of a high Tamman temperature stabilizing oxide, e.g. Al<sub>2</sub>O<sub>3</sub>,<sup>7,10,22,26,29</sup> SiO<sub>2</sub>,<sup>7,9</sup> TiO<sub>2</sub>,<sup>30</sup> CeO<sub>2</sub>,<sup>14</sup> MgAl<sub>2</sub>O<sub>4</sub><sup>21,31</sup> and ZrO<sub>2</sub>.<sup>13,23,27</sup> have been proposed. Indeed, these oxides have shown to increase the stability of iron based oxygen carriers over multiple cycles by reducing FeO<sub>x</sub>/Fe particle sintering.<sup>23</sup> Among the investigated oxides, Al<sub>2</sub>O<sub>3</sub> is particularly interesting owing to its relatively low cost, high Tamman temperature of ~885 °C and high mechanical resistance.<sup>32–34</sup> However, Al<sub>2</sub>O<sub>3</sub> can react with iron oxide forming the spinel

phase FeAl<sub>2</sub>O<sub>4</sub> (hercynite) which leads to a decay in the H<sub>2</sub> yield due to the limited capacity of FeAl<sub>2</sub>O<sub>4</sub> to split water at the typical operating conditions of conventional CL (700–1000 °C).<sup>10,22,26,35</sup> Hydrogen production using iron aluminate-based materials has been proposed for solar driven thermochemical cycles that cycles between spinel iron based solid solutions through an oxygen vacancy mediated mechanism; however, this is limited to high steam-to-hydrogen ratios and the H<sub>2</sub> capacity does not exceed 0.5 mmol H<sub>2</sub> per g FeAl<sub>2</sub>O<sub>4</sub>.<sup>36–38</sup>

Approaches to prevent the formation of FeAl<sub>2</sub>O<sub>4</sub> during redox operation have included the addition of alkali or alkali earth metal oxides to the oxygen carrier, yet the mechanisms behind the mitigation of FeAl<sub>2</sub>O<sub>4</sub> formation remains elusive.<sup>23,34,39</sup> In particular, the effect of the addition of sodium on the redox performance of Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> based oxygen carriers is controversially discussed and the underlying mechanisms at the atomic scale that would explain the improved macroscopic redox performance of such oxygen carriers are currently not well understood. For instance, a previous study proposed that formulations based on Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O and/or MgO could potentially hinder 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> phases that are thermodynamically more stable.<sup>31</sup> Indeed, X-ray powder diffraction (XRD) analysis confirmed the presence of NaAlO<sub>2</sub> and MgAl<sub>2</sub>O<sub>4</sub> phases in the two studied oxygen carriers with compositions Na : Al : Fe = 0.25 : 0.25 : 0.50 and Na : Mg : Fe : Al = 0.20 : 0.15 : 0.28 : 0.37 (molar ratios). However, it was found that only MgAl<sub>2</sub>O<sub>4</sub> effectively hindered the formation of inactive FeAl<sub>2</sub>O<sub>4</sub> while NaAlO<sub>2</sub> only partially prevented its formation. This was explained by the gradual replacement of Al<sup>3+</sup> by Fe<sup>3+</sup> in NaAlO<sub>2</sub> (NaAl<sub>1-y</sub>Fe<sub>y</sub>O<sub>2</sub>) during redox cycling leading to the formation of free Al<sub>2</sub>O<sub>3</sub> that subsequently reacts with FeO<sub>x</sub> to form FeAl<sub>2</sub>O<sub>4</sub>. A further study found that the addition of sodium in concentrations below 5 wt% stabilizes the reactivity of Fe<sub>2</sub>O<sub>3</sub>, yet the structure of the oxygen carriers was not studied in detail.<sup>20,40</sup> Typically, X-ray powder diffraction (XRD) has been applied to identify the phases present in the oxygen carrier, however, this analysis fails at describing the local structure of the materials and it is insensitive to amorphous phases and phases in low concentration. Thus, the fine structural features of Na-modified Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> oxygen carriers remain elusive.

As discussed above, a difficulty in improving our understanding of the effect of the addition of sodium to Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> on its redox behaviour is the lack of knowledge of the atomic-scale structure of these materials. Thus, this work aims at shedding light on the structure-performance relationships of sodium modified Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> oxygen carriers for H<sub>2</sub>-production by addressing the following questions: (i) how is the atomic scale structure of Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> based oxygen carriers modified by the addition of Na? (ii) what is the Na, Al and Fe environment in the oxygen carrier? and (iii) how does the redox performance relate to the oxygen carriers' structure? To address these questions we performed a detailed structural and redox analysis of sodium modified Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> and a sodium free benchmark utilizing XRD and X-ray absorption spectroscopy (XAS) data at the Fe, Al and Na K-edges.



## Experimental

### Synthesis of the oxygen carriers

Fe<sub>2</sub>O<sub>3</sub>:Al<sub>2</sub>O<sub>3</sub> and Na-modified Fe<sub>2</sub>O<sub>3</sub>:Al<sub>2</sub>O<sub>3</sub> oxygen carriers were synthesized using a sol-gel method<sup>22</sup> with the following compositions: (i) Fe : Al molar ratio: 0.66 : 0.34 (75 wt% Fe<sub>2</sub>O<sub>3</sub>, 25 wt% Al<sub>2</sub>O<sub>3</sub>), referred to as FeAl; (ii) Na : Fe : Al = 0.02 : 0.66 : 0.32 (76 wt% Fe<sub>2</sub>O<sub>3</sub>, 23 wt% Al<sub>2</sub>O<sub>3</sub>, 1 wt% Na<sub>2</sub>O), referred to as FeAlNa1; and (iii) Na : Fe : Al 0.11 : 0.64 : 0.25 (76 wt% Fe<sub>2</sub>O<sub>3</sub>, 19% wt% Al<sub>2</sub>O<sub>3</sub> and 5 wt% Na<sub>2</sub>O), referred to as FeAlNa5, (Table S1†). In a typical synthesis, aluminum isopropoxide (Al(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>, purity ≥ 98 wt%) was mixed with water and the mixture was hydrolysed for two hours at 75 °C under constant stirring. Nitric acid was used to peptize the slurry. The required amount of the iron and sodium precursors, iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, purity ≥ 98 wt%) and sodium nitrate (NaNO<sub>3</sub>, purity ≥ 99 wt%) respectively, were mixed with water to obtain a 1 M solution that was added subsequently to the slurry and refluxed for 12 h at 90 °C. The molar ratio of Al<sup>3+</sup> : H<sub>2</sub>O : H<sup>+</sup> was fixed to 0.5 : 50 : 0.07. The resulting gel was dried at 100 °C overnight to remove the solvents. A xerogel was obtained after calcination at 900 °C for 2 hours. The calcined materials were crushed and sieved to a particle size range of 300–425 μm for further characterization.

### Reference materials for structural characterization

The following reference materials for XAS analysis were synthesized. Na-β-Al<sub>2</sub>O<sub>3</sub>, with a molar ratio of Na : Al = 1 : 11 (NaAl<sub>11</sub>O<sub>17</sub>, *P6<sub>3</sub>/mmc* space group<sup>39</sup>) was synthesized by mixing stoichiometric amounts of γ-Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> followed by calcination at 1350 °C for 6 hours. Na-γ-Al<sub>2</sub>O<sub>3</sub> (sodium dispersed at the surface of γ-Al<sub>2</sub>O<sub>3</sub>) with a molar ratio of Na : Al = 1 : 15 was synthesized by wet impregnation of a solution of NaNO<sub>3</sub> (purity > 99 wt%) onto γ-Al<sub>2</sub>O<sub>3</sub>. The material was dried at 100 °C in an oven overnight, followed by calcination at 900 °C for 2 h. In addition, commercially available α-Al<sub>2</sub>O<sub>3</sub> (Alfa Aesar, aluminum oxide, α-phase, 99.9% metal basis) and γ-Al<sub>2</sub>O<sub>3</sub> (Alfa Aesar, aluminum oxide, γ-phase, 99.98% metal basis) were utilized as reference materials. The XRD pattern of the references Na-β-Al<sub>2</sub>O<sub>3</sub>, Na-γ-Al<sub>2</sub>O<sub>3</sub>, α-Al<sub>2</sub>O<sub>3</sub> and γ-Al<sub>2</sub>O<sub>3</sub> are provided in Fig. S1.† All of the materials were exposed to ambient conditions before characterization. Thus, ambient humidity likely hydrated the surface of all studied oxygen carriers and references, and possibly also the interlayers in the case of Na-β-Al<sub>2</sub>O<sub>3</sub>.

### Characterization of the oxygen carriers

The crystalline phases of the calcined and cycled oxygen carriers were studied by XRD, using a PANalytical Empyrean X-ray powder diffractometer, equipped with a X'Celerator Scientific ultra-fast line detector and Bragg-Brentano HD incident beam optics using Cu K<sub>α</sub> radiation (45 kV and 40 mA). A secondary monochromator was employed to suppress unwanted fluorescence originating from iron. Patterns were collected in the range of 2θ = 5–90°, with a step size of 0.016° s<sup>-1</sup> and a total acquisition time of 4 h. Rietveld refinements were performed using FullProf software.<sup>41</sup>

The local structure of the materials was characterized by XAS at the Fe, Na and Al K-edges. The Na K-edge and Al K-edge XAS measurements were carried out at the Phoenix II, elliptical undulator beamline at the Swiss Light Source (SLS) at the Paul Scherrer Institute (PSI), Switzerland. In a typical experiment a small quantity of material was pressed onto an indium foil and fixed to a copper plate.<sup>42</sup> XAS measurements were performed in fluorescence mode. The X-ray fluorescence signal was detected using a 1-element Si-drift diode detector SDD (Ketek, Germany). Total electron yield was also collected in the case of Al K-edge measurements. In samples with a high content of absorbing atoms, *i.e.* non-diluted and not thin enough samples, the fluorescence detected XAS signal was corrected due to self-absorption. The current of the incoming beam (*I*<sub>0</sub>) was measured using the total electron yield signal from a 0.5 μm thin polyester foil that was coated with a 50 nm thick layer of nickel. The beam passed through this foil approximately 1 m upstream of the sample in a vacuum chamber held at ~10<sup>-6</sup> mbar. Self-absorption correction in the Al K-edge spectra was applied. The Fe K-edge XAS spectra were collected at the BM31 beamline at the ESRF, Grenoble, France. The samples were ground, mixed with cellulose to optimize for X-ray absorption and pelletized. The data were collected in transmission mode using a Si(111) double crystal monochromator. Post-processing, self-absorption correction and analysis of the XAS data were performed using the Demeter 0.9.20 software package.<sup>43</sup>

High-resolution field emission scanning electron microscopy (Zeiss ULTRA 55 plus) was employed to visualize the surface morphology of the oxygen carriers before and after cyclic redox tests. Furthermore, elemental mapping of the synthesized materials was achieved *via* a Leo Gemini 1530 SEM equipped with an energy dispersive X-ray spectrometer (EDX). A FEI Talos F200X operated at 200 kV was used in both transmission electron microscopy (TEM) and scanning TEM (STEM) modes, with a probe size of approximately 0.8 nm. The instrument is equipped with SuperX EDX comprising four SDD detectors. The STEM/EDX analyses were complemented with atomic number sensitive, high angle annular dark field (HAADF) STEM.

The surface area as well as the pore size distribution of the calcined oxygen carriers were determined using a Quantochrome NOVA 4000e N<sub>2</sub> adsorption analyser. The samples were degassed at 300 °C for two hours prior to the acquisition of the N<sub>2</sub> isotherms. The Brunauer-Emmett-Teller (BET)<sup>44</sup> and Barrett-Joyner-Halenda (BJH)<sup>45</sup> models were used to calculate, respectively, the surface area and the pore size distribution of the materials.

### Redox performance

Cyclic redox experiments were performed in a packed bed reactor, as described in detail in a previous study.<sup>23</sup> The operating temperature was 800 °C to ensure a sufficiently high reduction rate allowing for a full reduction of Fe<sub>2</sub>O<sub>3</sub> to Fe in the set time. A typical redox cycle consists of the following steps: (i) reduction in CO (10 vol% CO in N<sub>2</sub>) for 15 minutes (1.5 L min<sup>-1</sup>), (ii) purging with N<sub>2</sub> (1.5 L min<sup>-1</sup>) for 1 minute, (iii)



oxidation of the reduced oxygen carrier with steam (23 vol% H<sub>2</sub>O in N<sub>2</sub>) for 7 minutes (1.94 L min<sup>-1</sup>), (iv) purging with N<sub>2</sub> (1.5 L min<sup>-1</sup>) for 1 minute, and (v) oxidation with 5 vol% O<sub>2</sub> in N<sub>2</sub> (2 L min<sup>-1</sup>) for 5 minutes.

## Results and discussion

First, we discuss the cyclic redox behaviour of the synthesized oxygen carriers to determine the effect of the addition of sodium on the redox performance of the materials. Subsequently, we probe in detail the structure of the oxygen carriers in the calcined state and after exposure to 15 redox cycles to establish structure–performance correlations.

### Cyclic redox performance

The cyclic redox performance of the oxygen carriers was assessed over 15 redox cycles in a packed bed reactor at 800 °C. In each cycle, the oxygen carriers were reduced in CO (10 vol% CO in N<sub>2</sub>) and oxidized first in H<sub>2</sub>O (23 vol% H<sub>2</sub>O in N<sub>2</sub>) and in a second step in O<sub>2</sub> (5 vol% O<sub>2</sub> in N<sub>2</sub>). The concentration profiles of the off gases for the different oxygen carriers during redox cycling are given in Fig. S2.† For each cycle, the H<sub>2</sub> yield during steam oxidation was calculated by integrating the molar flow rate of H<sub>2</sub> produced (obtained from off-gas concentration profiles) with respect to time by using eqn (7):<sup>21</sup>

$$N_{\text{H}_2} = \dot{N}_{\text{N}_2} \times \int \frac{y_{\text{H}_2}}{1 - y_{\text{H}_2}} dt \quad (7)$$

where  $N_{\text{H}_2}$  is the number of moles of H<sub>2</sub> produced,  $\dot{N}_{\text{N}_2}$  is the molar flow rate of N<sub>2</sub>, and  $y_{\text{H}_2}$  is mole fraction of H<sub>2</sub> in the gas leaving the packed bed.

The H<sub>2</sub> yield expressed as mmol H<sub>2</sub> per g of oxygen carrier as a function of cycle number is given in Fig. 1. The H<sub>2</sub> yield of FeAl decreased rapidly over 15 cycles from 12.7 mmol H<sub>2</sub> per g oxygen carrier in the first cycle, to 11.1 mmol H<sub>2</sub> per g oxygen carrier in the fifth cycle and to 6 mmol H<sub>2</sub> per g oxygen carrier in the fifteenth cycle. The addition of sodium enhanced the redox stability of FeAlNa1 and increased the H<sub>2</sub> yield compared to FeAl; however, from the eighth redox cycle onwards also for this material the H<sub>2</sub> yield started to decrease. A more pronounced stabilization effect was observed in FeAlNa5. The H<sub>2</sub> yield of FeAlNa5 was stable over 15 redox cycles and was close to the theoretically expected value of 13.3 mmol g<sup>-1</sup> oxygen carrier. These results show that the introduction of sodium has a large impact on the cyclic behaviour of Al<sub>2</sub>O<sub>3</sub> stabilized, Fe<sub>2</sub>O<sub>3</sub>-based oxygen carriers.

The effect of sodium on the reduction kinetics of iron oxide can be evaluated using the gas concentration profiles obtained in the first cycle. The concentration profiles of the off gases given in Fig. S3a,† show that FeAlNa1 and FeAlNa5 have very comparable reduction rates. The fractional conversion of the oxygen carriers tested are only marginally different in the first reduction step, which indicates that the presence of sodium does not affect appreciably the reduction kinetics of Fe<sub>2</sub>O<sub>3</sub>. The reduction characteristics of the oxygen carriers were assessed further by CO and H<sub>2</sub>-TPR experiments (Fig. S4†). In the case of

steam oxidation, in the first cycle the conversion of FeAl was faster than the conversion of FeAlNa1 and FeAlNa5 indicating that the addition of sodium does not have a positive impact on oxidation kinetics (Fig. S5†). Over cycling, the water splitting kinetics decreased for the deactivating oxygen carriers (Fig. S6†). However, the overall oxidation duration of FeAlNa5 is fairly unaffected by the cycle number.

To obtain insight into the origin of the improved redox stability of FeAlNa1 and FeAlNa5 compared to FeAl, the morphological and structural characteristics of the calcined and cycled materials (15 cycles) were probed by XRD, XAS and STEM/EDX.

### Structure of the calcined and cycled oxygen carriers by XRD and XAS

**Calcined oxygen carriers.** XRD analysis confirms that the main crystalline component in all of the calcined materials is hematite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Fig. 2a and Table S2†). Additionally,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (corundum) is observed in FeAl and FeAlNa1. In the case of FeAlNa5, there are also reflections due to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> observable; however, with a very weak intensity. In addition, FeAlNa5 contains a third phase, *i.e.* Na- $\beta$ -Al<sub>2</sub>O<sub>3</sub> (*P6<sub>3</sub>/mmc* space group, Fig. 2b).<sup>46</sup> Rietveld refinement allowed us to quantify the fraction of the crystalline phases in the oxygen carriers and to determine the cell parameters of these phases. The unit cell parameters of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are reported in Table S2† and did not change (within the experimental error) upon the addition of sodium (Fig. 2 and Table S2†). The fact that the cell parameters are invariant with the addition of Na suggests that sodium is not incorporated into the crystal structures of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> or  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The determined cell parameters of Na- $\beta$ -Al<sub>2</sub>O<sub>3</sub> ( $a = b = 5.6385$  Å and  $c = 22.816$  Å) is in a good agreement with previous studies.<sup>46–48</sup> The weight fractions of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in the calcined materials were determined as 27, 23 and 3 wt% for FeAl and FeAlNa1 and FeAlNa5 respectively, *i.e.* the fraction of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> decreased with increasing Na content. For FeAl and FeAlNa1,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> balanced the phase composition of the oxygen carriers, amounting to, respectively, 73 and 77 wt%  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. For FeAlNa5, the refined phase composition was 82 wt%  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, 15 wt% Na- $\beta$ -Al<sub>2</sub>O<sub>3</sub> and 3 wt%  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The presence of Na- $\beta$ -Al<sub>2</sub>O<sub>3</sub> in FeAlNa1 was not evidenced by XRD, yet this might be due to limitations of XRD in determining phases of low concentrations and/or poor crystallinity. To obtain further insight into the effect of the addition of sodium on the phase composition and structure of the oxygen carriers, we turned to an element specific technique X-ray technique, *i.e.* XAS at the Fe, Na and Al K-edges.

First, we analysed the local environment around iron. Fe K-edge XANES (X-ray absorption near edge structure) spectra of the calcined oxygen carriers are provided in Fig. 2d. The spectra of all of the oxygen carriers contain the same features as the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> reference. The EXAFS (extended X-ray absorption fine structure) functions and the corresponding Fourier transforms (FT) are given in Fig. S7† and further confirm that the local environment around Fe corresponds to the local Fe environment in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in all three calcined materials. Hence, the XAS



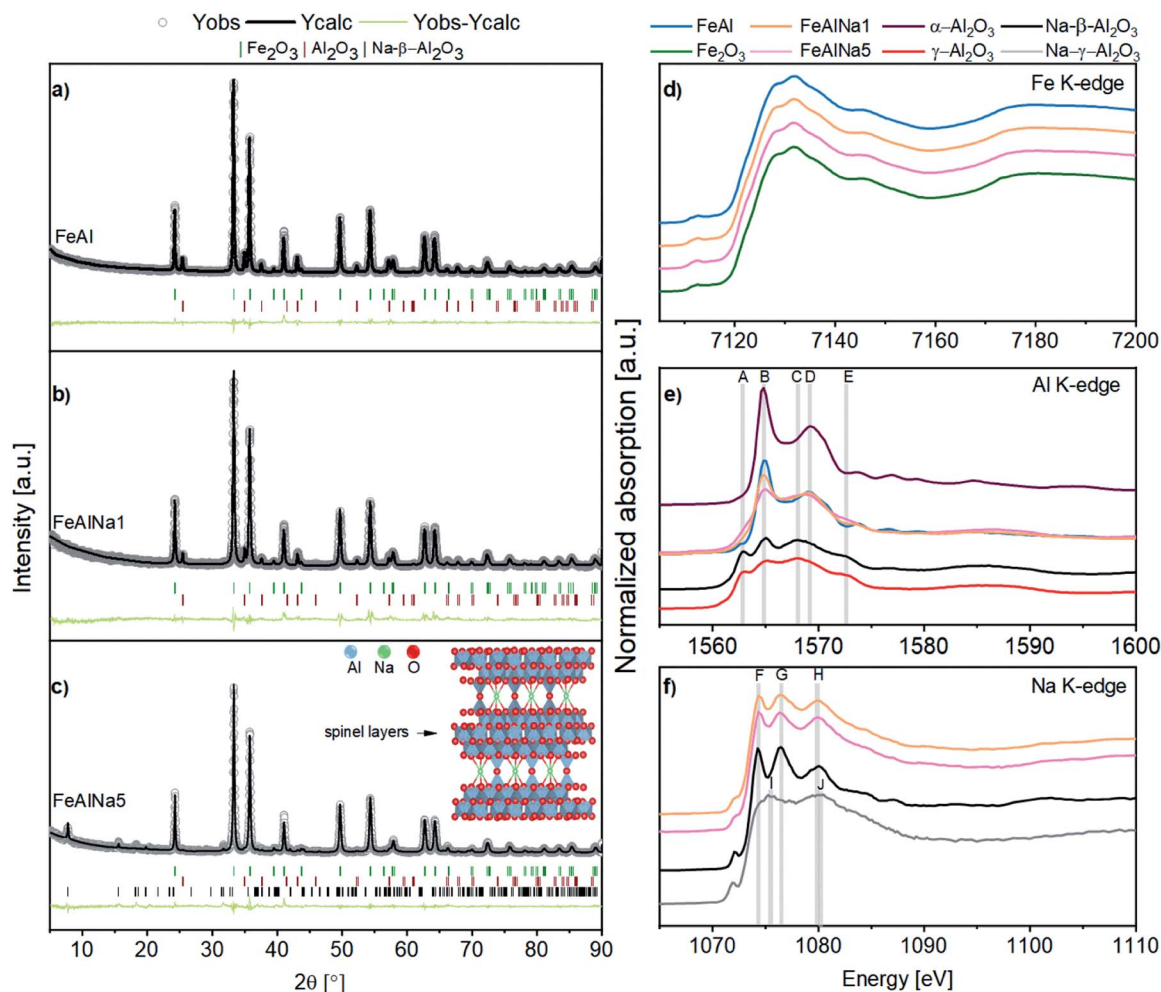


Fig. 2 (a)–(c) XRD patterns of the calcined oxygen carriers and the corresponding Rietveld refinements. The inset in (c) sketches the crystal structure of Na- $\beta$ -Al $_2$ O $_3$  containing layers of  $\gamma$ -alumina that are connected by bridging oxygen and sodium ions. XANES spectra at the (d) Fe K-edge, (e) Al K-edge, (f) Na K-edge of the calcined oxygen carriers and reference materials.

data confirm that the local environment of Fe is not affected by the presence of sodium. Importantly, it also shows that there is no formation of a solid solution or mixed oxide between Fe $_2$ O $_3$  and Al $_2$ O $_3$  upon calcination at 900 °C.

Fig. 2e displays the Al K-edge XANES spectra of the oxygen carriers and reference materials. To interpret these XANES data we will first discuss the XANES data of the reference materials  $\alpha$ -Al $_2$ O $_3$ ,  $\gamma$ -Al $_2$ O $_3$  and Na- $\beta$ -Al $_2$ O $_3$ . The crystal structure of  $\alpha$ -Al $_2$ O $_3$  is described by a hexagonal unit cell with Al in an octahedral coordination. The corresponding XANES spectrum (Fig. 2e) exhibits a doublet peak in the white-line region, with a sharp intense peak at 1565 eV (labelled as B), and a broader feature at 1568 eV (labelled as D), typical for Al in an octahedral coordination and in agreement with previously data.<sup>49,50</sup> The reference  $\gamma$ -Al $_2$ O $_3$  has a defect spinel type structure, in which Al atoms occupy both octahedral and tetrahedral sites.<sup>51</sup> In the XANES spectrum of  $\gamma$ -Al $_2$ O $_3$ , features A, B, C and E are observed at 1563, 1565, 1568 and 1573 eV, respectively. In  $\gamma$ -Al $_2$ O $_3$  feature B is considerably less intense than in  $\alpha$ -Al $_2$ O $_3$  and feature C has been attributed to tetrahedrally coordinated Al.<sup>52,53</sup> Na- $\beta$ -Al $_2$ O $_3$  is a layered structure containing  $\gamma$ -Al $_2$ O $_3$  layers that are linked by

sodium and oxygen atoms (inset in Fig. 2c).<sup>54,55</sup> The fact that the Al K-edge XANES spectrum of Na- $\beta$ -Al $_2$ O $_3$  exhibits similar features as  $\gamma$ -Al $_2$ O $_3$  confirms the presence of  $\gamma$ -Al $_2$ O $_3$  layers in Na- $\beta$ -Al $_2$ O $_3$ .<sup>54</sup>

Next, we investigate the Al environment in the three oxygen carriers. The Al K-edge XANES spectrum of FeAl shows features B and D, indicating that Al $^{3+}$  is in an octahedral coordination similar to  $\alpha$ -Al $_2$ O $_3$ ,<sup>49</sup> in line with XRD. With increasing sodium content, the intensity of feature B decreases, which implies that the fraction of  $\alpha$ -Al $_2$ O $_3$  in the material decreases with increasing sodium content. In agreement with our previous XRD analysis is the fact that the Al K-edge XANES spectrum of FeAlNa1 is dominated by features due to  $\alpha$ -Al $_2$ O $_3$ . On the other hand, in FeAlNa5 features A, C and E are prominent which is indicative of the presence of spinel-type  $\gamma$ -Al $_2$ O $_3$  or Na- $\beta$ -Al $_2$ O $_3$  (according to XRD). Features A, C and E are also present in FeAlNa1, but with a considerably lower intensity. Hence, our XANES results indicate that FeAlNa1 and FeAlNa5 contain a mixture of  $\alpha$ -Al $_2$ O $_3$  and a spinel-type Al $_2$ O $_3$  phase. While  $\alpha$ -Al $_2$ O $_3$  is the main Al-based phase in FeAlNa1, Na- $\beta$ -Al $_2$ O $_3$  (or  $\gamma$ -Al $_2$ O $_3$ ) is the main Al-containing phase in FeAlNa5. Na- $\beta$ -Al $_2$ O $_3$  and  $\gamma$ -Al $_2$ O $_3$  share



the same Al K-edge features, yet combining the information of XRD and Na-K-edge XAS (*vide infra*), we assign the observed features to Na- $\beta$ -Al<sub>2</sub>O<sub>3</sub> rather than to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Lastly, we assess the Na environment in the oxygen carriers and reference materials. The Na K-edge XANES spectrum of Na- $\beta$ -Al<sub>2</sub>O<sub>3</sub> exhibits three main peaks labelled as F, G and H, located at 1074, 1076 and 1080 eV, respectively (Fig. 2f). To the best of our knowledge, this is the first experimentally collected Na K-edge spectrum of Na- $\beta$ -Al<sub>2</sub>O<sub>3</sub>. The spectrum of Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (*i.e.* the reference material prepared by wet impregnation of a solution of NaNO<sub>3</sub> onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) shows features different to Na- $\beta$ -Al<sub>2</sub>O<sub>3</sub> and are labelled I (1075 eV) and J (1080 eV) (Fig. S8†). These Na K-edge XANES features of Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are assigned to Na ions dispersed on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (in a solvated state).<sup>55</sup> Thus, using Na K-edge XANES we can distinguish between two different Na environments: (i) a Na- $\beta$ -Al<sub>2</sub>O<sub>3</sub> like environment, *i.e.* Na that is located between layers of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layers (ordered) and (ii) a Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> like environment in which Na is located on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (surface Na<sup>+</sup>). The Na K-edge XANES spectra of FeAlNa1 and FeAlNa5 exhibit features F, G and H at, respectively 1074.4 eV (A), 1076.4 eV (B) and 1080.2 eV (C), suggesting a similar Na local environment in these two calcined oxygen carriers as in Na- $\beta$ -Al<sub>2</sub>O<sub>3</sub> (Fig. 2f). The presence of Na- $\beta$ -Al<sub>2</sub>O<sub>3</sub> in FeAlNa5 aligns with XRD results. The absence of diffraction peaks due to Na- $\beta$ -Al<sub>2</sub>O<sub>3</sub> in FeAlNa1 is possibly linked to its small quantity in FeAlNa1. However, we noticed

that the features F, G and H in the Na K-edge XANES spectra of FeAlNa1 and FeAlNa5 are less intense compared to the reference Na- $\beta$ -Al<sub>2</sub>O<sub>3</sub>. This is possibly due to the presence of two different Na environments in the calcined oxygen carriers. This observation led us to propose that the Na K-edge XANES spectra of the oxygen carriers can be fitted by a linear combination of Na in an environment of Na- $\beta$ -Al<sub>2</sub>O<sub>3</sub> and surface Na<sup>+</sup> in the form of Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Indeed, linear combination fitting yielded Na to be *ca.* 60% in a Na- $\beta$ -Al<sub>2</sub>O<sub>3</sub> environment and 40% in a Na- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> type environment in both FeAlNa1 and FeAlNa5 (Fig. S9†).

**Cycled oxygen carriers.** To probe in depth the effect of sodium-containing phases on the redox stability of the Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> system the structures of the oxygen carriers that have undergone 15 redox cycles were also characterized by XRD and XAS. The cycled oxygen carriers were analysed in their reduced state as it has been argued that the presence of sodium hinders the formation of inactive hercynite during reduction.<sup>10,22,26</sup>

The cycled materials (labelled with *\_cyc*) exhibit dominant Bragg reflections due to fcc-Fe (Fig. 3a). However, the presence of magnetite (Fe<sub>3</sub>O<sub>4</sub>), wuestite-FeO (only in FeAl) and hercynite (spinel FeAl<sub>2</sub>O<sub>4</sub>) in FeAl<sub>cyc</sub> and FeAlNa<sub>cyc</sub> points to an incomplete reduction. Importantly, the XRD pattern of FeAlNa5<sub>cyc</sub> does not show peaks due to FeAl<sub>2</sub>O<sub>4</sub>, but peaks due to Na- $\beta$ -Al<sub>2</sub>O<sub>3</sub> (Fig. 3a), indicating that Na- $\beta$ -Al<sub>2</sub>O<sub>3</sub> is stable under redox conditions. The XANES spectra and FT-EXAFS functions of the three cycled oxygen carriers are shown in Fig. 3 and S10,† respectively.

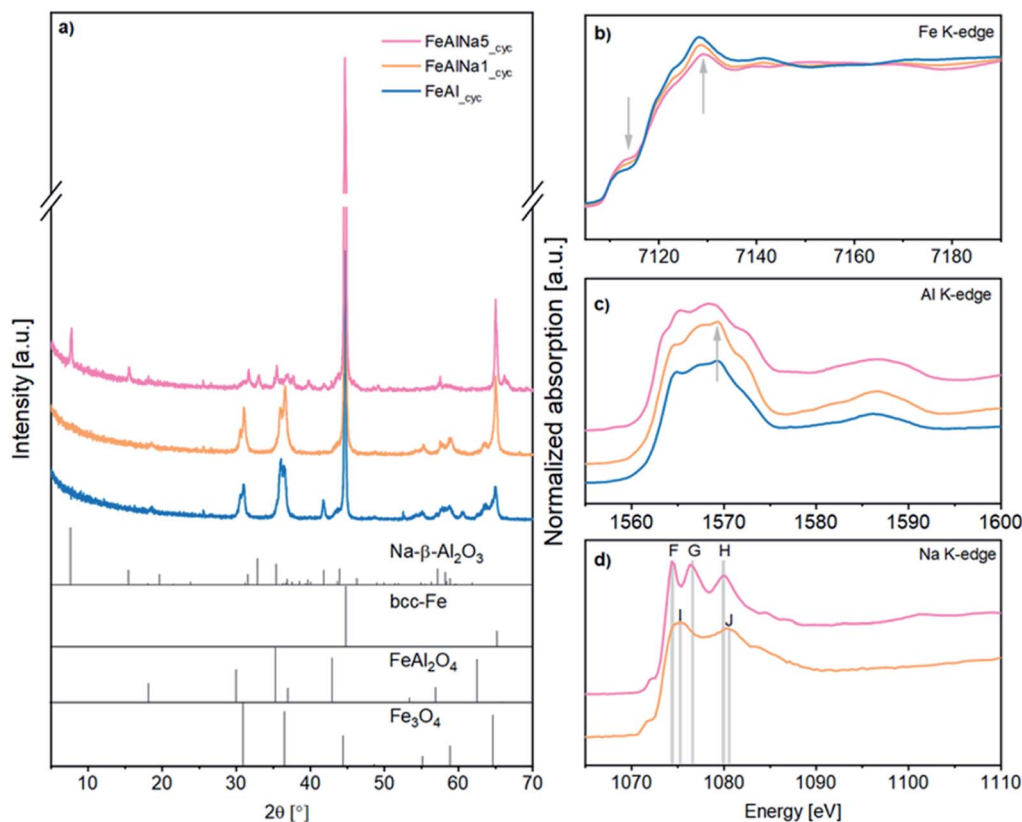


Fig. 3 (a) XRD patterns of the cycled oxygen carriers (15 redox cycles, reduction step) together with simulated diffraction patterns of the reference materials. XANES spectra at the (b) Fe K-edge (the arrows show the direction of change), (c) Al K-edge (the arrows point to distinct features in FeAlNa<sub>cyc</sub> and FeAlNa<sub>cyc</sub>); and (d) Na K-edge of the cycled materials.



From the increase in the intensity of the white line it is clear that the degree of reduction followed the order  $\text{FeAl}_{\text{cyc}} < \text{FeAlNa1}_{\text{cyc}} < \text{FeAlNa5}_{\text{cyc}}$ . The Fe K-edge XANES spectra (Fig. 3b) of the oxygen carriers were fitted by a linear combination of an Fe foil, FeO and  $\text{FeAl}_2\text{O}_4$  and yielded 48, 79 and 94 wt% metallic  $\text{Fe}^0$  in, respectively,  $\text{FeAl}_{\text{cyc}}$ ,  $\text{FeAlNa1}_{\text{cyc}}$  and  $\text{FeAlNa5}_{\text{cyc}}$ . These results confirm that in  $\text{FeAlNa5}$  the formation of  $\text{FeAl}_2\text{O}_4$  during reduction is hindered and iron oxide can be reduced almost completely over 15 redox cycles. To some extent, there is also a stabilization effect in  $\text{FeAlNa1}$ , yet the formation of  $\text{FeAl}_2\text{O}_4$  could not be avoided fully. This is in line with the drop in the hydrogen yield of  $\text{FeAlNa1}$  with cycle number.

Turning to the analysis of the Al K-edge XANES data of the cycled oxygen carriers, we did not observe any signatures due to  $\alpha\text{-Al}_2\text{O}_3$  in any of the cycled oxygen carriers, instead features characteristic of spinel type phases are present. The Al K-edge XANES spectrum of  $\text{FeAlNa5}_{\text{cyc}}$  (Fig. 3c) shows the same characteristic features as the  $\text{Na-}\beta\text{-Al}_2\text{O}_3$  reference (Fig. 2e). This indicates that during redox cycling the small fraction of  $\alpha\text{-Al}_2\text{O}_3$  that was initially present in calcined  $\text{FeAlNa5}$  transforms fully to  $\text{Na-}\beta\text{-Al}_2\text{O}_3$ . Comparing the spectrum of  $\text{FeAlNa5}_{\text{cyc}}$  with the spectra of  $\text{FeAl}_{\text{cyc}}$  and  $\text{FeAlNa1}_{\text{cyc}}$  revealed a more intense feature at ca. 1569.6 eV for  $\text{FeAl}_{\text{cyc}}$  and  $\text{FeAlNa1}_{\text{cyc}}$  (marked with an arrow in Fig. 3c). This feature can be attributed to the substitution of Al sites by Fe in a spinel structure in analogy to the spinel  $\text{MgAl}_2\text{O}_4$ <sup>52</sup> which is isostructural to  $\text{FeAl}_2\text{O}_4$ . Hence, consolidating with our XRD and Fe K-edge XAS results, the feature at 1569.6 eV in the Al K-edge XANES spectra of  $\text{FeAl}_{\text{cyc}}$  and  $\text{FeAlNa1}_{\text{cyc}}$  is attributed to the formation of  $\text{FeAl}_2\text{O}_4$ .

The Na K-edge XANES spectra of the cycled materials are shown in Fig. 3d. We observe that in  $\text{FeAlNa5}_{\text{cyc}}$  the local environment of Na in the form of  $\text{Na-}\beta\text{-Al}_2\text{O}_3$  is preserved during redox cycling. This is evidenced by the presence of the three features F, G and H in  $\text{FeAlNa5}_{\text{cyc}}$ . Linear combination fitting of the spectrum of  $\text{FeAlNa5}_{\text{cyc}}$  yields 71% of Na in a  $\text{Na-}\beta\text{-Al}_2\text{O}_3$  framework and 29% of Na in the form of surface Na ( $\text{Na-}\gamma\text{-Al}_2\text{O}_3$  type). Hence, the fraction of Na in a  $\text{Na-}\beta\text{-Al}_2\text{O}_3$ -type environment in  $\text{FeAlNa5}$  increases with redox cycling, in line with Al K-edge XANES analysis. On the other hand, the Na K-edge XANES spectrum of  $\text{FeAlNa1}_{\text{cyc}}$  exhibits, compared to  $\text{FeAlNa5}$ , a different change in the Na environment with redox cycling. The three sharp features (labelled F, G and H) in calcined  $\text{FeAlNa1}$  are not detected in  $\text{FeAlNa1}_{\text{cyc}}$  (Fig. S11<sup>†</sup>). Instead a broader doublet (features I and J) at 1075 and 1080.5 eV appears after redox cycling, indicative that  $\text{FeAlNa1}_{\text{cyc}}$  closely resembles the spectrum of the  $\text{Na-}\gamma\text{-Al}_2\text{O}_3$  reference. This change in the local environment of Na upon redox cycling, indicates that in  $\text{FeAlNa1}$  Na is initially present in a  $\text{Na-}\beta\text{-Al}_2\text{O}_3$  like environment (in the layered structure), but migrates and disperses on the material's surface during redox cycling.

### Morphology and elemental mapping of the calcined and cycled carriers

The morphology of the freshly calcined oxygen carriers, as probed by electron microscopy is affected only marginally by the addition of sodium (Fig. S12<sup>†</sup>). The calcined oxygen carriers

$\text{FeAl}$ ,  $\text{FeAlNa1}$  and  $\text{FeAlNa5}$  were composed of particles with an average grain size of  $\sim 100 \pm 20$  nm (based on the analysis of 50 particles). The particle size of  $\text{Fe}_2\text{O}_3$ , calculated using STEM-EDX maps of the calcined oxygen carriers (Fig. S13<sup>†</sup>), was in the range of 80–120 nm for the oxygen carriers tested ( $119 \pm 33$  nm,  $135 \pm 36$  nm and  $87 \pm 40$  nm for  $\text{FeAl}$ ,  $\text{FeAlNa1}$  and  $\text{FeAlNa5}$ , respectively). The weight composition of the materials as determined by SEM/EDX (Table S1<sup>†</sup>) are in good agreement with the nominal compositions of the oxygen carriers. The elemental mapping of the oxygen carriers revealed that the sol-gel synthesis led to a high dispersion of Fe, Na and Al, indicating that the different phases were highly dispersed in the materials (Fig. S14<sup>†</sup>). The calcined oxygen carriers  $\text{FeAl}$ ,  $\text{FeAlNa1}$  and  $\text{FeAlNa5}$  have similar BET surface areas and BJH pore volumes (Table S1<sup>†</sup>).

HAADF-STEM images and the corresponding EDX maps of Fe, Al and Na are given in Fig. 4. In the calcined materials  $\text{FeAl}$ ,  $\text{FeAlNa1}$ , and  $\text{FeAlNa5}$ , discrete  $\text{Fe}_2\text{O}_3$ - and  $\text{Al}_2\text{O}_3$ -rich particles are formed, and Na is distributed evenly in  $\text{FeAlNa1}$ . In  $\text{FeAlNa5}$ , the EDX signals of Al and Na overlap, which is in line with the outcome of the XRD and XAS analysis (Fig. 2) pointing to the formation of a  $\text{Na-}\beta\text{-Al}_2\text{O}_3$  phase. Similarly, the EDX maps of  $\text{FeAl}_{\text{cyc}}$  and  $\text{FeAlNa1}_{\text{cyc}}$  show overlapping signals of Fe and Al, which are in agreement with the formation of the spinel  $\text{FeAl}_2\text{O}_4$  as determined by XRD and XAS. No such overlap is observed in  $\text{FeAlNa5}_{\text{cyc}}$ , which features discrete Al- and Fe-rich particles. Furthermore, the overlapping signals of Na and Al in  $\text{FeAlNa5}_{\text{cyc}}$  provide further evidence for the formation of  $\text{Na-}\beta\text{-Al}_2\text{O}_3$  as determined by the XRD and XAS analyses.

### Structure–performance relationships

Combining the results of the cyclic redox tests, with our XRD, XAS and HAADF-STEM-EDX analyses we can propose the following structure–performance correlations. The reaction of  $\alpha\text{-Al}_2\text{O}_3$  with  $\text{Fe/FeO}_x$  during redox cycling leads to the formation of (inactive)  $\text{FeAl}_2\text{O}_4$  that in turn correlates with a rapid decay in the  $\text{H}_2$  yield in  $\text{FeAl}$ . The high redox stability of  $\text{FeAlNa5}$  correlates with the formation of  $\text{Na-}\beta\text{-Al}_2\text{O}_3$  and the absence of  $\alpha\text{-Al}_2\text{O}_3$  in this oxygen carrier. The formation of  $\text{Na-}\beta\text{-Al}_2\text{O}_3$  in  $\text{FeAlNa5}$  hinders effectively the formation of  $\text{FeAl}_2\text{O}_4$  during repeated redox cycles, leading in turn to a material with a stable hydrogen yield. The  $\text{Na-}\beta\text{-Al}_2\text{O}_3$  phase is stable at reductive and oxidative environments and is highly dispersed within the  $\text{Fe/FeO}_x$  matrix. The oxygen carrier with a lower Na content, *i.e.*  $\text{FeAlNa1}$ , shows a dominating presence of  $\alpha\text{-Al}_2\text{O}_3$  and a small fraction of  $\text{Na-}\beta\text{-Al}_2\text{O}_3$  initially freshly calcined state. Such a phase composition can only partially stabilize the oxygen carrier. Indeed, in  $\text{FeAlNa1}$ , Na is initially present in two environments *i.e.* as  $\text{Na-}\beta\text{-Al}_2\text{O}_3$  and dispersed as surface Na. During the redox cycling of  $\text{FeAlNa1}$ , all of the  $\alpha\text{-Al}_2\text{O}_3$  reacts with  $\text{FeO}_x$  forming  $\text{FeAl}_2\text{O}_4$ , while sodium is found in a non-crystalline form (dispersed at the surface of the particle). A schematic representation of the phase evolution during redox cycling is given in Fig. S15.<sup>†</sup> Therefore, our study points to the critical role of the layered  $\text{Na-}\beta\text{-Al}_2\text{O}_3$  phase in stabilizing the hydrogen yield of  $\text{Al}_2\text{O}_3$ -stabilized,  $\text{Fe}_2\text{O}_3$  based oxygen carriers.



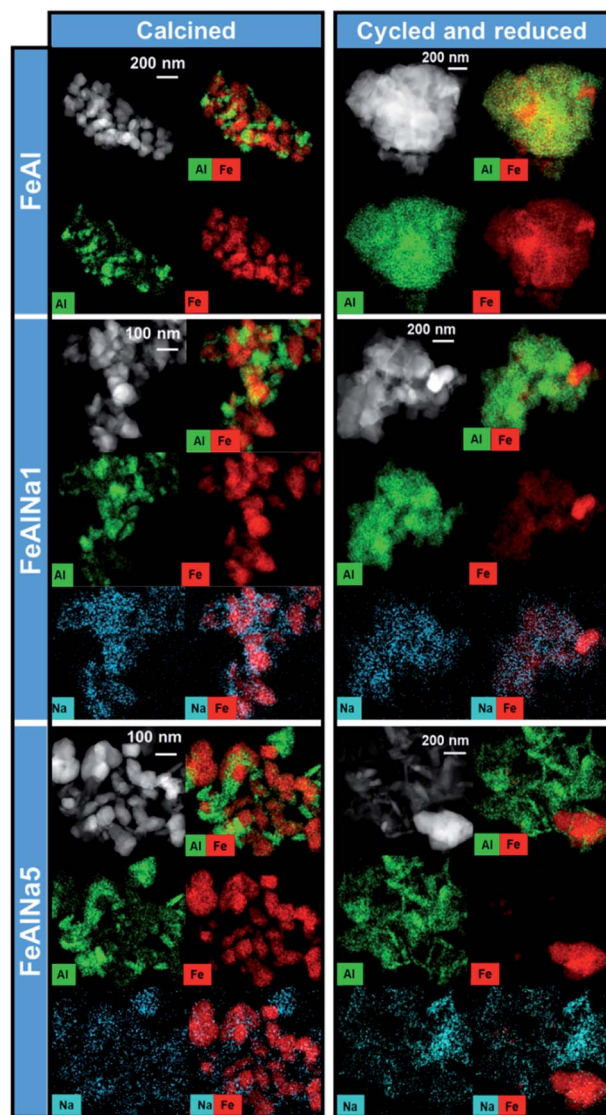


Fig. 4 HAADF images and elemental maps (STEM-EDX) of the calcined oxygen carriers and after cycling experiments (15 cycles, reduction step).

## Conclusions

In this work, we probe the effect of the addition of sodium to  $\text{Fe}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$ -based oxygen carriers, on their redox stability, phase composition and phase dynamics over redox cycles. Application of XRD, XAS at the Al, Na and Fe K-edges and STEM/EDX to the freshly calcined and cycled materials allowed us to draw the following conclusions:

(i)  $\alpha$ - $\text{Al}_2\text{O}_3$  reacts with  $\text{Fe}/\text{FeO}_x$  during redox cycling leading to the formation of  $\text{FeAl}_2\text{O}_4$ ; the formation of which correlates directly with the rapid decrease in the  $\text{H}_2$  yield of an oxygen carrier.

(ii) Depending on the loading of sodium in the oxygen carrier, sodium can be found in a crystalline  $\text{Na-}\beta$ - $\text{Al}_2\text{O}_3$  phase or at the surfaces of the particles.

(iii) Na in the environment of the layered structure  $\text{Na-}\beta$ - $\text{Al}_2\text{O}_3$  effectively stabilizes the redox performance of an oxygen carrier, while surface sodium cannot prevent fully material deactivation.

This work, demonstrates how probing of the local and average structure, such as multi edge XAS analysis in combination with XRD and electron microscopy allows for the formulation of structure–performance correlations. In addition, this work showcases the application of XAS in the tender X-ray region (Na and Al K-edges) that have not been investigated extensively particularly in the field of chemical looping and can, therefore, be of interest to the broader functional materials community. Our study brings fundamental understanding of the role of  $\text{Na-}\beta$ - $\text{Al}_2\text{O}_3$  for the stabilization of  $\text{Fe}_2\text{O}_3$ -based oxygen carriers. Nonetheless, further studies that explore different reducing gases (such as  $\text{CH}_4$ ), operation temperatures and long-term stability (>100 cycles) are required.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The authors would like to acknowledge the Swiss National Science Foundation (406640\_136707) and the Swiss Office of Energy (BFE, SI/500652) for financial support. This project has received partial funding from the European Union's Horizon 2020 research and innovation program (grant agreement No. 800419). This publication was created as part of NCCR Catalysis, a National Centre of Competence in Research funded by the Swiss National Science Foundation. We also thank Scientific Centre for Optical and Electron Microscopy (ScopeM) for providing training and access to scanning electron microscopes. The authors are grateful to the Swiss Light Source (SLS) at the Paul Scherrer Institute (Villigen, Switzerland), for providing beamtime at the PHOENIX beamline, and to the European Synchrotron Facility (ESRF) and the Swiss-Norwegian beamline (SNBL at ESRF) for providing beamtime for XAS measurements. We thank Dr Felix Donat for the insightful discussions on thermodynamic analysis.

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