Enhanced Performance of Alkali Metal Doped Fe$_2$O$_3$ and Fe$_2$O$_3$/Al$_2$O$_3$ Composites As Oxygen Carrier Material in Chemical Looping Combustion

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Supporting Information

ABSTRACT: In this study alkali metal doped Fe$_2$O$_3$ and Fe$_2$O$_3$/Al$_2$O$_3$ composite oxygen carriers were synthesized from spray pyrolysis, and the reactivity and stability as oxygen carrier materials were evaluated in a fixed bed reactor for 50 isothermal redox cycles using CH$_4$ as the fuel. We find that both Fe$_2$O$_3$ and Fe$_2$O$_3$/Al$_2$O$_3$ composite showed reactivity degradation over multiple cycles, with a clear phase separation between Fe and Al, in the composites. In contrast, alkali metal doping (~5 mol %) with Na, K, and Cs was found to stabilize the reactivity of the Fe$_2$O$_3$ over the 50 redox cycles and prevent phase Fe—Al separation in the composite. Methane to CO$_2$ selectivity was found to be relevant to the dopant type, which decreased in the order of dopant type K, Cs, and Na. The best performing alkali metal, K, enhanced long-term stability significantly, with no observed degradation in kinetics and total conversion performance in the methane step as well as reduced coke formation. Adding an alumina matrix to K doped Fe$_2$O$_3$ helped promote CO$_2$ generation as well as minimize coking and was found to be the best performing material.

1. INTRODUCTION

Chemical looping combustion (CLC) involves a two-step process in which metal oxides as the oxygen carrier (OC) replacing air in order to avoid direct contact between fuel and air.$^1$ Current primary interests in CLC lie in the potential advantages of burning hydrocarbons or coal in a nitrogen-free environment so as to enable more efficient/economical CO$_2$ sequestering as well as avoid NO$_x$ formation.$^{2,3}$ However, finding good oxygen carriers is one of the major challenges in any widespread implementation of CLC.$^4$ The important properties of oxygen carriers are high reactivity to both reduction and oxidation as well as high mechanical stability and recyclability over multiple cycles, low cost, and environmentally benign.$^5,6$ Metal oxides including copper-, iron-, nickel-, and mixed-oxide have been studied; however, Fe-based oxygen carriers while economical have shown a relatively slow reduction rate and a propensity for physical and chemical degradation over time.$^7,8$ Fe$_2$O$_3$ can be sequentially reduced to Fe$_2$O$_4$, FeO, and finally Fe, with different CO$_2$ conversions.$^{9,10}$ The important advantages of an iron-based material coupled with its high melting point and being environmentally benign have continued to maintain interest in these materials. In an effort to enhance an active surface area, pore volume, sintering resistance, long-term stability and recyclability, support materials including Al$_2$O$_3$, SiO$_2$, MgO, TiO$_2$, ZrO$_2$, and CeO$_2$ have been employed.$^{4,9,11,12,13,14}$ The performance improvement with supported OCs was often attributed to enhanced intraparticle gaseous diffusivity as well as electronic or O$_2$ mobility considering the reactions between OC and fuel are gas—solid or solid—solid reactions.$^{13—15}$

In order to enhance the reactivity of Fe$_2$O$_3$, we have referred to the fact that alkali metal doping of catalysts has been known to improve selectivity and activity or prolong the lifetime of metal/metal oxide catalysts.$^{16,21,24}$ Specifically, activity decreases in the order of Cs, K, Na, and Li, attributed to the decreasing size, polarization, and electronegativity.$^{23}$ While strictly speaking the oxygen carrier is considered a reactant and not a catalyst, one might expect that some of the same principles that improve the catalyst may also improve oxidation performance. With that logic, in this study we demonstrate that K doped Fe$_2$O$_3$ offers significant improvement in performance, both cycling and a lower coke formation potential in the reduction step with methane, while other alkali metals are not as effective. Further enhancement is seen when alumina is included to make composite alkali doped particles. In both cases, no long-term degradation in performance is observed.

2. APPROACH

All oxygen carriers studied were in-house synthesized by aerosol spray pyrolysis.$^{25}$ Briefly speaking, the system consists of an atomizer (to produce aerosol droplets), silica-gel diffusion drier (to remove solvent), a high temperature furnace, and a sample collector (to collect nanoparticles). The aerosol of precursor solution is generated using a collision-type nebulizer with an initial droplet diameter is about 1 μm, which is dried by passing through a diffusion dryer. The aerosol is then passed through a tube furnace operated at 600 °C to create the solid particle with a residence time of ~1 s. Particles exiting the aerosol reactor are then collected on a 0.4 μm DTTP Millipore filter. In order to thermally decompose all nitrates completely, all particles were annealed at 750 °C for 1 h before the CLC test.

The precursors for the Fe$_2$O$_3$, Al$_2$O$_3$ and alkali metal components were Fe(NO$_3$)$_3$, 9H$_2$O, Al(NO$_3$)$_3$, 9H$_2$O, and MO$_3$ (M = Na, K, Cs), respectively, at a total concentration of 0.2 M. For the samples tested in this paper, a 5 mol % of alkali metal relative to Fe was added, in each case, such as 4.8 mol % K, 95.2 mol % Fe$_2$O$_3$ (Fe$_2$O$_3$·K), 4.8 mol % Cs,
95.2 mol % \( \text{Fe}_2\text{O}_3 \) (\( \text{Fe}_2\text{O}_3 \cdot \text{Cs} \)), 50 mol % \( \text{Fe}_2\text{O}_3 \)/50 mol % \( \text{Al}_2\text{O}_3 \) (1Fe1Al), 2.6 mol % K, 48.7 mol % \( \text{Fe}_2\text{O}_3 \)/48.7 mol % \( \text{Al}_2\text{O}_3 \) (1Fe1Al·K), 2.6 mol % Na, 48.7 mol % \( \text{Fe}_2\text{O}_3 \)/48.7 mol % \( \text{Al}_2\text{O}_3 \) (1Fe1Al·Na), 1.3 mol % Na, 1.3 mol % Na, 48.7 mol % \( \text{Fe}_2\text{O}_3 \)/48.7 mol % \( \text{Al}_2\text{O}_3 \) (1Fe1Al·1K1Na).

The reactivity of oxygen carriers was tested in a vertically oriented fixed bed reactor placed in an electrically heated isothermal furnace. While industrial practice probably favors the use of fluidized-beds, there are examples of designs for full scale fixed bed reactors for CLC.\textsuperscript{27,28} From a laboratory stand-point, fixed bed studies are widely used due to the simplicity of operation and the small samples that can be utilized.\textsuperscript{7,12,31,32,37,40} This latter point was of particular interest to us since our focus is on materials synthesis and rapid screening. Readers will also note that our materials are nanoscale. Obviously this length scale is not practical in fluidized beds, however particles of the type described here are easily generated by spray pyrolysis methods at various sizes.\textsuperscript{29} Finally it is possible to construct microsized particles comprised of nanoparticles by spray induced aggregation that offers
accessible surface areas that greatly exceed the corresponding external surface area.\textsuperscript{30}

About 200 mg of sample material was used for each test. The quartz flow reactor has a length of 61 cm, with a 1 cm i.d. as described in Figure 1. The particles were first annealed at the reaction temperature for 1 h and then exposed alternatively to 11\% methane for 2 min and 20\% oxygen for 5 min simulating the CLC system. Argon is introduced for 300 s after each period to avoid oxygen and methane mixing during the shift between oxidation and reduction. In total, 50 cycles were achieved in this test.

MKS mass flow controllers (MFCs) for the three gases were regulated by a Labview VI program. The reactor effluent was characterized by a mass spectrometer (Stanford Research UGA 300) operating with a mass resolution <0.5 atomic mass unit (amu) at 10\% of peak height and a detection limit <1 ppm. Argon was used as an inert internal standard to determine the volume change of gaseous reactants and products during the reaction so as to assign concentrations. By varying the flow rates of CH\textsubscript{4} and O\textsubscript{2} with a fixed Ar flow rate, calibrations of the mass spectrometer for different gases with different concentrations were accomplished. Crystal structures of OCs were characterized by X-ray diffraction (XRD) with a Bruker Smart1000 using Cu K\textalpha\ radiation. Transmission electron microscopy (TEM) and elemental mapping were performed using a field-emission transmission electron microscope (JEOL JEM 2100F). Scanning electron microscopy (SEM) and energy-dispersive X-ray (SEM-EDX) results were obtained by Hitachi SU-70 SEM.

3. RESULTS AND DISCUSSION

A differential mobility analyzer (DMA) coupled with a condensation particle counter (CPC) described in our previous work was utilized to obtain the size distribution of the as-synthesized particles.\textsuperscript{31} As shown in Figure 2c, the Fe\textsubscript{2}O\textsubscript{3} particle diameter peaks at 84 nm without K and 87 nm with 5 mol \% K, implying that particle size effects can be ignored in any comparison. Similar results were obtained with other dopants (Na, Cs).

The multiple-cycle test in the fixed bed reactor examines the reactivity and stability of the selected oxygen carriers. Figure 3a illustrates the temporal dependence of oxygen carrier reduction with the CH\textsubscript{4} reaction to CO\textsubscript{2} of neat Fe\textsubscript{2}O\textsubscript{3} sample at the first cycles. Normalized time is the real time normalized by the pulse length. The conversion–time plot shows a sigmoidal shape, indicating that the gas–solid reaction may proceed following the JMA model.\textsuperscript{17,18} Since this study primarily focuses on total yield, selectivity, and cycling stability, the data presented subsequently are under conditions of steady conditions (i.e., long times) so that temperature dependence of kinetics cannot be evaluated. Figure 3b shows that adding potassium results in a slight improvement in the kinetics without changing final yield. This is important since any long-term stability improvements through the addition of potassium should not ultimately degrade kinetic performance. Assuming that both cases share the same reaction order, the temporal conversion plots yield a reaction rate for the potassium added case roughly twice that for the neat iron oxide.

Figure 4 shows the performance behavior at different temperatures for unmixed (Figure 4a,c) and K added OCs’ multicycle performance (Figure 4b,d). Theoretically, the conversion from Fe\textsubscript{2}O\textsubscript{3} to Fe\textsubscript{3}O\textsubscript{4} should give a CO\textsubscript{2} yield of 0.52 mmol/g from Fe\textsubscript{2}O\textsubscript{3} to FeO, 1.56 mmol/g and from Fe\textsubscript{2}O\textsubscript{3} to Fe, 4.69 mmol/g. Equilibrium calculation shows that Fe\textsubscript{2}O\textsubscript{3} under methane leads to 100\% CO\textsubscript{2} but that subsequent partial reduction to FeO gives a mixture of CO and CO\textsubscript{2}.\textsuperscript{11,35} Our experimental results could not reliably quantify this point due to relative high mass (N\textsubscript{2}) background in our

Figure 4. CO\textsubscript{2} yield per gram of Fe\textsubscript{2}O\textsubscript{3} for (a) Fe\textsubscript{2}O\textsubscript{3}, (b) Fe\textsubscript{2}O\textsubscript{3}K (95.2 mol \% Fe\textsubscript{2}O\textsubscript{3} with 4.8 mol \% K), (c) 1Fe1Al (50 mol \% Fe\textsubscript{2}O\textsubscript{3}/50 mol \% Al\textsubscript{2}O\textsubscript{3}), (d) 1Fe1AI-K (2.6 mol \% K 48.7 mol \% Fe\textsubscript{2}O\textsubscript{3}/48.7 mol \% Al\textsubscript{2}O\textsubscript{3}) at 750 °C, 850 °C, and 950 °C.
mass spectrometer. It is clear that for the first cycle of the neat Fe₂O₃ (Figure 4a) and 50 mol % Fe₂O₃/50 mol % Al₂O₃ (Figure 4c) samples, the Fe₂O₃ got converted to Fe₃O₄ after the CH₄ step. Also, it demonstrates that from Figure 4a that for pure Fe₂O₃, performance degrades steadily after each cycle, which has also been reported by others and is one of the problems plaguing many OCs. Addition of aluminum nitrate to create an alumina stabilizing matrix (Figure 4c) for the Fe₂O₃ exhibited essentially identical behavior to the neat Fe₂O₃ oxide case, implying that at least under the synthetic strategy pursued here, the alumina offered no advantages. For both cases before K+ addition (Figure 4a,c), CO₂ generation degraded to almost one-third its first cycle at the 50th cycle. The addition of K however, shown in Figure 4b,d stabilized the Fe₂O₃ (Figure 4a) and 50 mol % Fe₂O₃/50 mol % Al₂O₃ for di
ference in performance detected. The degradation may be attributed to the decreasing oxygen-ion transport within the lattice or a reduction in the oxygen binding energy. Meanwhile, adding K+ to the Fe₂O₃/Al₂O₃ composite also helped modify the degradation problem (Figure 4d). To be more specific, 2.6 mol % K 48.7 mol % Fe₂O₃ 48.7 mol % Al₂O₃ OCs were also tested, with no difference in performance detected. The alkali metals have also been shown to improve selectivity, reduce coking, or prolong lifetime of metal/metal oxide catalysts for various reactions. At least for the conversion, addition of aluminum oxide stabilizer appears to be no advantage, but it is included here because of a subsequent discussion on selectivity.

Because one of the primary motivations of CLC today is CO₂ sequestering, selectivity is extremely important, specifically with respect to coking, which may occur from a number of side reactions including the Boudouard reaction (reaction 1) and methane pyrolysis (reaction 2).

\[2\text{CO} \rightarrow \text{C} + \text{CO}_2 \]  

(1)

\[\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \text{ (pyrolysis)} \]  

(2)

The second reaction is endothermic while the first reaction is exothermic. Furthermore, methane decomposition is thermodynamically preferred at high temperatures, while the Boudouard reaction is favored at low temperatures. Carbon formation comes from the two reactions mentioned above and then burned away in the oxidation step. Therefore, the amount of CO₂ observed in the oxidation step can be directly used to determine the extent of coke formation in the methane step. The two different side reactions can be differentiated by the amount of hydrogen generated during the methane step, as it results only from methane decomposition (reaction 2). As the amount of hydrogen generated during the methane step was double the amount of CO₂ generated during the oxidation step, we can conclude that methane decomposition is the primary side reaction. We define CO₂ selectivity (based on the amount of CO₂ measured during the fuel step) as

\[\chi_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{n_C + n_{\text{CO}_2}} \]

where \(n_{\text{CO}_2}\) is determined directly during the fuel step, and \(n_C\) is measured indirectly by the amount of CO₂ measured during the oxidation step. Thus, the selectivity represents the amount of methane that is reacting with the OCs rather than decomposing. \(\chi_{\text{CO}_2}\) of different OCs at 750 °C for 50 cycles is shown in Figure 6. It is evident that addition of alkaline metals improves CO₂ selectivity against coking and that potassium works best in the context of selectivity. The addition of the alumina support provides further improvement. This 48.7 mol % Fe₂O₃/48.7 mol % Al₂O₃/2.6 mol % K material clearly offers superior performance in both reactivity stability and CO₂ selectivity. This result implies that alkali metals promote oxidation over pyrolysis although the mechanism is not well understood.

Phase identification of oxygen carriers was determined using XRD (Table S1 in the Supporting Information), indicating that all iron oxides were \(\gamma\)-Fe₂O₃ or Fe₃O₄. Even though the samples...

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**Figure 5.** CO₂ yield per gram of Fe₂O₃ for different OCs at 750 °C as a function of cycle number.
were obtained after the CH₄ step cooled down to room temperature in Ar, the high temperature reduced phase gets easily oxidized and thus all XRD patterns gave peaks assigned to Fe₂O₃ and four reduced samples (OC samples after the CH₄ step) gave peaks of Fe₃O₄. No signals for K−Fe may come from two reasons: (1) K−Fe forms very fine particles beyond the limit of XRD detection and (2) K−Fe forms solid solutions. From HR-TEM results (Figures S2 and S3 in the Supporting Information), the second one is more reasonable since K−Fe stayed homogeneously distributed in the particle. Also, the XPS and deconvolution results for the Fe 2p core-level (Figure S4 in the Supporting Information) of 4.8 mol % K 95.2 mol % Fe₂O₃ sample showed very similar patterns and main peaks of Fe 2p3/2 around 710.8 eV, which demonstrates no chemical bonding between K and Fe, which means that K⁺ may move around in the Fe₂O₃ crystal as ion interstitials. XRD analysis on the Al₂O₃ supported sample has two major phases: Fe₂O₃ and Al₂O₃, with no mixed Fe−Al−O phase formation and no mixed Fe−K−Al−O phase formation is detected (e.g., KFeO₂). Moreover, XPS also gave the same information.

The SEM micrographs of the OCs are shown in Figure 7. Consistent with the size distribution measurements in Figure 2, as produced particles from spray pyrolysis were spherical ~0.1–1 μm. After ~1 h thermal annealing at 750 °C, particles maintained their spherical shapes. After 50 cycles (15 h), particles clearly showed evidence of some sintering, although for all but the smallest particles the characteristic length scales are still nominally the same. The Na doped sample (not shown) was essentially indistinguishable from the K counterparts despite the fact that the reactivity was much lower. It is worth noticing that all particles displayed similar amounts of sintering, regardless of alkali metal doping. It can be implied that sintering does not account for the reactivity differences.

TEM elemental mapping is shown in Figures 8 and 9, for the as prepared 50 mol % Fe₂O₃/50 mol % Al₂O₃(Figure 8a,c), after multicycles at 750 °C (Figure 8b,d) and 2.6 mol % K 48.7 mol % Fe₂O₃/48.7 mol % Al₂O₃ after multicycle CLC at 750 °C. Figure 8a,c show that in the as-produced material, the iron is homogeneously dispersed within the alumina matrix but that after CLC (Figure 8b,d), considerable morphological changes have occurred accompanied with a significant phase separation between Fe and Al. This is also consistent with the fact as shown in Figure 4 that the Al additions to iron oxide have minimal performance effects and show the same general trend of decreasing activity with time. However, 2.6 mol % K 48.7 mol % Fe₂O₃/48.7 mol % Al₂O₃ composite, as shown in Figure 9, clearly stabilizes the structure from both morphological sintering effects but also phase separation between Al and Fe.
Similar results (Figure S1 in the Supporting Information) were achieved with the Na sample after 50 cycles, but recall that the Na containing sample did not perform well. The mapping results indicate that the alkaline metal helps to retard phase separation within the alumina support, which may account for the long-term stability of 2.6 mol % K 48.7 mol % Fe₂O₃/48.7 mol % Al₂O₃ OC relative to the nascent iron oxide and little alkaline metal loss. Potassium ions movement may exist as a binder for Fe–Al, thus preventing phase separation between the two. This result indicates that the alkaline effect here is more than the catalytic surface effect; it is a whole particle effect. Additional TEM images in the Supporting Information (Figures S2 and S3) indicate that Cs, however, did not stay in iron oxide and was found to phase separate to the surface of the OC surface. This separation may be attributed to the larger size of the Cs⁺ (~181 pm) ion compared to K⁺ (~152 pm) and Na⁺ (~116 pm) as well as its higher ion polarization. Previous catalysis studies have seen similar trends in the tendency for Cs phase separation.

Our experimental approach is not amenable to identify the root cause of the potassium effect; however, unlike a catalysis which is a pure surface effect, we are driving the OC within the whole particle and thus we expect whatever the alkali metal effect it must involve more than surface effects. This may involve changing oxygen-ion transport within the lattice or a reduction in the oxygen binding energy. The fact that Na with its lower electronegativity performs worse is consistent with this, with the Cs, because of its instability within the lattice not providing any useful insights on this point. The stability of iron within the alumina implies that the alkali metal (both K and Na) stiffens the alumina matrix from moving around and offers a stable path for oxygen transport to the surface which may help to explain the improved selectivity (i.e., reduction in coking).

4. CONCLUSIONS

We demonstrate that addition of potassium to iron oxide nanoparticles during synthesis can significantly enhance its performance in long-term CLC tests of methane oxidation. This was however not true for Na or Cs addition. In the latter, Cs addition was not incorporated within the lattice but was found to phase separate into small Cs particles at the surface of the iron oxide. Synthesis of particles with an alumina matrix was found to have a minimal effect for nascent iron oxide performance but when added in combination with potassium yielded the best performance in terms of long-term stability as well as CO₂ selectivity with respect to coking.

ASSOCIATED CONTENT

Supporting Information

XRD identifications of different OCs sample, TEM images, and XPS and deconvolution results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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