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Effect of support on redox stability of iron oxide for chemical looping conversion of methane

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ABSTRACT

The chemical looping processes utilize lattice oxygen in oxygen carriers to convert carbonaceous fuels in a cyclic redox mode while capturing CO_2. Typical oxygen carriers are composed of a primary oxide for active lattice oxygen storage and a ceramic support for enhanced redox stability and activity. Among the various primary oxides reported to date, iron oxide represents a promising option due to its low cost and natural abundance. The current work investigates the effect of support on the cyclic redox performance of iron oxides as well as the underlying mechanisms. Three ceramic supports with varying physical and chemical properties, i.e. perovskite-structured $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}O_3$, fluorite-structured CeO_2, and spinel-structured $MgAl_2O_4$, are investigated. The results indicate that the redox properties of the oxygen carrier, e.g. activity and long-term stability, are significantly affected by support and iron oxide interactions. The perovskite supported oxygen carrier exhibits high activity and stability compared to oxygen carriers with ceria support, which deactivate by as much as 75% within 10 redox cycles. The high stability of perovskite supported oxygen carrier is attributable to its high mixed ionic–electronic conductivity. Deactivation of ceria supported samples results from solid-state migration of iron cations and subsequent enrichment on the oxygen carrier surface. This leads to agglomeration and lowered lattice oxygen accessibility. Activity of $MgAl_2O_4$ supported oxygen carrier is found to increase during redox cycles in methane. The activity increase is a consequence of surface area increase caused by filamentous carbon formation and oxygen carrier fragmentation. While higher redox activity is desired for chemical looping processes, physical degradation of oxygen carriers can be detrimental.

1. Introduction

CO_2 emissions from the oxidation of fossil fuels can lead to unintended consequences of climate change [1,2]. Thus, novel approaches for CO_2 capture, utilization, and sequestration (CCUS) are highly desired. The chemical looping strategy offers a potentially viable option for efficient carbonaceous fuel conversion with reduced carbon footprints. In the chemical looping process, an oxygen carrier is reduced and oxidized in a cyclic manner to convert carbonaceous fuels into separate streams of concentrated carbon dioxide and carbon-free products such as heat/electricity or hydrogen [3–9]. During the reduction step, the oxygen carrier, a.k.a. redox material, donates its lattice oxygen to the fuel while getting reduced, thereby converting the carbonaceous fuels to a gaseous mixture of carbon dioxide and water vapor. In the subsequent oxidation step(s), the oxygen deprived oxygen carrier is regenerated with gaseous oxygen and/or steam, resulting in heat and/or hydrogen products [4,10]. Since the effectiveness of chemical looping processes is largely affected by the performance of the oxygen carrier, i.e. its physical robustness, redox activity, stability, cost, etc., oxygen carrier development and optimization is a key area for chemical looping research.

A key component of an oxygen carrier is its active material or primary oxide, which directly participates in the abovementioned cyclic redox operations. Resulting from their suitable thermodynamic properties, oxides of first row transition metals such as iron, nickel, copper, manganese, and/or cobalt are among the most frequently used primary oxides for chemical looping applications [3,11–16]. With most unsupported metal oxides showing diminishing redox activities over multiple redox cycles [3,17], a support, which is typically selected from ceramic materials with relatively stable structures, is usually added to the primary oxide to improve its long-term redox performance. Among the various primary

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oxides, iron oxide(s) is particularly attractive due to its low cost, high oxygen capacity, and abundance [3,18]. In addition, reduced iron and wustite can be effective for hydrogen production through water-splitting [5,12,19]. A key challenge for iron oxide based oxygen carrier development is to obtain oxygen carriers with improved activity and recyclability. To address such a challenge, addition of supports including Al_2O_3, $MgAl_2O_4$, CeO_2, TiO_2, and YSZ have been investigated [11,15,20–25]. While supports can improve the activity and stability of iron based oxygen carriers [3,11,20,24,26,27], relatively few studies have investigated the roles of support for overall oxygen carrier performance.

Activity changes, i.e. deactivation or activation, for supported iron oxide over multiple redox cycles have been reported [28–31]. Bleeker et al. reported deactivation of iron oxide in a steam-iron process [29]. The authors attributed deactivation to the decrease in surface area by iron (oxide) sintering. In contrast, iron oxide ores such as ilmenite are shown to activate during the chemical looping combustion (CLC) processes, possibly due to an increase in porosity over cyclic redox reactions [28,30]. Li et al. investigated TiO_2 supported iron oxides [32,33]. Slight increase in activity of the oxygen carrier was observed with decreasing surface area and porosity through redox cycles. Based on inert marker experiments and density function theory (DFT) calculations, the authors proposed that high conductivities of electrons and lattice oxygen (O^{2-}) of the supported sample are responsible for improved redox activity of the supported iron oxide. A recent study by Galinsky et al. have indicated that a mixed ionic–electronic conductive (MIEC) lanthanum strontium ferrite (LSF) support significantly improves the redox activity and stability of iron oxide based oxygen carriers [34]. The activity increase is believed to result from the excellent mixed conductivity of the LSF perovskite support. Shafiefarhood et al. examined a novel strategy of covering iron oxide with an LSF shell for methane partial oxidation [35]. The LSF shell helped to achieve high activity, stability, and syngas selectivity over duration of 100 redox cycles. Similar to LSF, ceria is a frequently studied mixed-conductive support [36–47]. Ceria supported iron oxide is reported to possess good redox stability for cyclic reactions with CH_4 (reduction) and steam (regeneration) [23]. Bhavsar and Veser deposited Fe_2O_3 onto synthesized ceria via an incipient wetness method [40]. The authors report stable activity of the Fe–Ce–O oxygen carrier in hydrogen at 800 °C with H_2 and CH_4 for 10 cycles. He et al. showed, at 850 °C in CH_4, that Ce–Fe–O with a Ce/Fe of 7/3 had stable activity between Fe_2O_3 and FeO phases over 20 redox cycles [42]. Contrast to the mixed-conductive perovskite and ceria, $MgAl_2O_4$ is a commonly encountered inert support [22,24,31,48–52]. Johansson et al. concluded that sintering temperature has a significant effect to the activity of Fe_2O_3 supported with $MgAl_2O_4$ [22]. They observed a slight increase in redox activity over 9–17 cycles in a 1:1 ratio of CH_4 and H_2O. The authors postulated that the activation is resulted from cracks and pore size change. To summarize, although a large number of supported iron oxides are tested, their deactivation/activation mechanisms have not been thoroughly investigated.

This article aims to investigate the roles of support on the redox activity and long-term stability of iron oxide based oxygen carriers. Three ceramic supports, i.e. perovskite-structured $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}O_3$, fluorite-structured CeO_2, and spinel-structured $MgAl_2O_4$ are investigated. Of these supports, $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}O_3$ and CeO_2 represent mixed-conductors with distinct crystal structures. $MgAl_2O_4$, on the other hand, is a frequently encountered inert support. Through detailed investigation of the relationship between oxygen carrier activation/deactivation and its support conductivity, surface and phase compositions, morphology, and surface area, general design principles for highly active and recyclable oxygen carriers are obtained.

Table 1
List of oxygen carriers synthesized.

Material	Method and composition
$Fe_2O_3:CeO_2$	SSR (3:7 molar ratio)
$Fe_2O_3:CeO_2$	Co-precipitation (3:7 molar ratio)
$Fe_2O_3:CeO_2$	Co-precipitation (4:6 molar ratio)
$Fe_2O_3:Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}O_3$	Citric acid (3:7 molar ratio)
$Fe_2O_3:MgAl_2O_4$	SSR (3:7 weight ratio)

2. Experimental methods

2.1. Oxygen carrier synthesis

Several oxygen carriers are synthesized using three approaches, i.e. solid state reaction (SSR), co-precipitation (CP), and citric acid (CA) methods. The oxygen carriers tested are shown in Table 1. Oxygen carrier samples prepared via SSR reactions are sintered at 1000–1050 °C while those prepared through CP and CA methods are sintered at 800–1000 °C. X-ray powder diffraction (XRD) is used to confirm the formation of the desired phases. A brief summary of these synthesis methods is given in the following section. Further details can be found in several references [34,53,54]. To ensure generality of the mechanistic findings, synthesis method and compositions of ceria and $MgAl_2O_4$ supported oxygen carriers are consistent with those reported in literature [22,24–26,35,36,39–47]. Activity and recyclability of the ceria based oxygen carriers in the current study are comparable, if not higher, than those reported in previous literatures under similar operating conditions (see Supplemental Fig. S3).

SSR samples are prepared by measuring calculated amounts of precursors Fe_2O_3 (99.9%, Noah Chemicals), CeO_2 (99.9%, Noah Chemicals), and $MgAl_2O_4$ (99.9%, Noah Chemicals) and placing them for 6 h in a planetary ball mill (XBM4X, Columbia International) at a rotation of 250 rpm. Following the milling step, the resulting mixture is pressed into pellets by a hydraulic press (YLJ-15T, MTI Corporation) at a pressure of 20 MPa. The pellets are then annealed, fractured, and sieved to powder (<150 μm) for testing.

The co-precipitation method involves taking calculated precursor nitrates $Fe(NO_3)_3{\cdot}9H_2O$ (98+%, Sigma–Aldrich) and $Ce(NO_3)_3{\cdot}6H_2O$ (99%, Sigma–Aldrich) into solution with deionized water. The solution is then mixed at 70 °C where a 10% ammonia solution is introduced drop wise to increase the pH of the solution to 9. The solution is allowed to precipitate at 70 °C for 1 h. It is then aged for 2 h. The resulting solids are subsequently filtered and washed thoroughly with deionized water and ethanol. They are then dried at 110 °C for 24 h. Calcination is performed at 300 °C to convert the hydroxide groups into oxides, and then the particles are crushed into powder and sintered for 6 h at 800 °C. A sintering temperature of 800 °C is used for CP sample to reproduce oxygen carriers reported in Ref. [53].

The citric acid method is used to prepare the $Fe_2O_3:Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}O_3$ oxygen carrier from Fe_2O_3 nanoparticles (<50 nm, Sigma–Aldrich), nitrate salts, and alkoxides. First, Fe_2O_3 nanoparticles are dispersed in ethanol via sonication. The solution is settled for 6 h to deposit the nanoparticles and to remove the upper liquid of the solution. The nanoparticles are re-dispersed in deionized water and sonicated. A second solution comprised of the precursors $Ca(NO_3)_2{\cdot}4H_2O$ (≥99.9%, Sigma–Aldrich), $Sr(NO_3)_2$ (ACS Reagent, Noah Chemicals), and $Ni(NO_3)_2{\cdot}6H_2O$ (Sigma–Aldrich) are placed into deionized water. Citric acid and EDTA are used as chelating agents. An ammonia solution is used to change the pH of the solution to 8. A third solution containing ethanol and citric acid is used to dissolve $Ti(OC_4H_9)_4$ (97%, Sigma–Aldrich). Solutions containing the metal ions are mixed thoroughly. The dispersed nanoparticles are