



Processing and characterization of Fe-based oxygen carriers for chemical looping for hydrogen production

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ABSTRACT

Until now various oxygen carrier particles have been proposed for use in chemical looping processes. Their chemical performance is determined not only by their composition and their microstructure/morphology but also by the reaction condition of the processes in which they are utilized. In the present work, iron based oxygen carriers supported on Al_2O_3 and MgAl_2O_4 were spray dried and heat treated to have a suitable morphology and sufficient mechanical properties for chemical looping. The MgAl_2O_4 -support was in situ generated from MgO and Al_2O_3 by reaction sintering. After physical characterization and determining their compressive strength the oxygen carriers were tested in the chemical looping reforming process for producing syngas in a lab-scale batch fluidized-bed reactor. The suitability of utilizing steam regeneration was investigated for both oxygen carriers by relating their chemical performance to their composition. It was shown that the Al_2O_3 -supported oxygen carrier deactivated after 9 cycles of steam regeneration because of the accumulation of an in-situ formed FeAl_2O_4 -phase due to an irreversible reaction between support and the active phase. This deactivation was successfully avoided by replacing the Al_2O_3 -support with MgAl_2O_4 . This $\text{Fe}_2\text{O}_3/\text{MgAl}_2\text{O}_4$ oxygen carrier could be subsequently regenerated by steam, making it suitable for chemical looping for hydrogen generation.

1. Introduction

Both Chemical Looping Combustion (CLC) and Chemical Looping Reforming (CLR) are processes where a fuel is (at least partially) oxidized by the lattice oxygen from an oxygen carrier based on metal oxides. Afterwards this lattice oxygen in the oxygen carrier is replenished by an oxidation with air or another oxidizing agent such as steam or CO_2 . In this way, the oxygen carrier acts as a selective means of transport for the oxygen which is transferred between the oxidizing agent and the fuel, and for the heat which is generated and consumed in the different chemical reactions which occur in the process. In this way a system is created in which the fuel (which can be gaseous, liquid or solid fuel) never comes into contact with the combustion air (Adanez et al., 2012). This is advantageous because the combustion gases are inherently separated from other components like N_2 from the flue gas (Mattisson et al., 2001) yielding a system without NO_x -formation (Hossain and de Lasa, 2008). The main difference between the CLC and CLR processes is their focus. CLC is used for heat generation by a total

combustion of the fuel into CO_2 and H_2O and CLR focusses on the production of H_2 or synthesis gas by oxidizing the fuel only partially. Different oxidative agents can be used for replenishing the lattice oxygen of the oxygen carriers. Although air is generally used for this purpose, also steam and CO_2 are being investigated because of their advantages of producing additional H_2 and CO respectively (Tang et al., 2015).

The oxygen carriers which are used to transfer oxygen from an oxidizing agent to the fuel in CLC and CLR are key issues in the performance of both chemical looping processes. They consist of metal oxides and must fulfill some requirements in order to be suitable for CLC or CLR. On the one hand this suitability intrinsically depends on the redox systems used. In this regard, several metal oxide systems are being widely investigated with Fe-based systems as very promising candidates because of their low cost and environmentally friendly behavior.

A lot of attention has been focused towards the development of Ni-based oxygen carriers due to their good reactivity, conversion and

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mechanical stability. However, their cost, susceptibility towards S-containing impurities (de Diego et al., 2014) and toxicity are key drivers to develop Ni-free materials. Although oxygen carriers based on Fe-oxides have weaker redox characteristics for CLC such as low methane conversion to CO₂ and H₂O and a low oxygen transport capacity for total combustion, they are promising because of their lower cost (Adánez-Rubio et al., 2014) and diminished impact on health and environment. Of all oxidation states (Fe₂O₃, Fe₃O₄, FeO and Fe), only the transformation from hematite (Fe₂O₃) to magnetite (Fe₃O₄) is applicable to CLC systems. When using the more reduced states of the iron oxides (i.e. FeO and Fe), the selectivity towards partial oxidation of methane becomes more favorable. These oxidation states are thus unsuitable for use in CLC (Abad et al., 2007a; Johansson et al., 2006; Tang et al., 2015) but instead more applicable to CLR. A final advantage of these iron based OC is their activity in the water splitting reaction (Kathe et al., 2016; Protasova and Snijkers, 2016; Tang et al., 2015) which will be used in this paper for OC regeneration accompanied with extra hydrogen production.

Because few pure metal oxides show good long term results, different supports are used to further improve the oxygen carrier capabilities related to their mechanical and chemical performance: Al₂O₃, MgAl₂O₄, SiO₂, TiO₂, kaolin (Cho et al., 2004), Zr-based and more recently perovskites (Chen et al., 2014; Galinsky et al., 2015; Rydén et al., 2008; Shafieifarhood et al., 2015) and CeO₂ (Bhavsar et al., 2016; Li et al., 2010; Wei et al., 2010; Yamaguchi et al., 2011; Zhu et al., 2014). These supports are used to provide a higher surface area for reaction, for their effects on the mechanical properties of the oxygen carriers, and also to increase the ionic conductivity of the solids (Abad et al., 2007a; Adanez et al., 2012).

In general all these supports exhibit a good reactivity for CLC, especially when oxidizing syngas or H₂. An exception is the Fe₂O₃/SiO₂ system which is incompatible because the reactivity of this material decreases significantly due to the formation of unreactive iron silicates (Zafar et al., 2006).

When utilized as a support material, Al₂O₃ and TiO₂ will also react with Fe²⁺ formed during the reduction of hematite with the formation of FeAl₂O₄ and FeTiO₃ (Chen et al., 2011). Unlike the silicates, these materials have the ability to be oxidized back by air. Furthermore, they show a good selectivity towards total oxidation of the fuel resulting in a higher available oxygen capacity for the total combustion in comparison with the pure iron oxides. FeAl₂O₄ and FeTiO₃ have a higher thermodynamic stability than the separate phases and thus modify the reduction and oxidation properties of the OC. For example, the oxidation of FeAl₂O₄ spinel to Fe₃O₄ (and Al₂O₃) will be more difficult than the oxidation of FeO to Fe₃O₄ (Svoboda et al., 2007). Therefore, the solid state reactions between the iron containing phases and the support are major causes for loss of reactivity of these materials during reaction.

Yttria-stabilized zirconia (YSZ) supported oxygen carriers have also shown some promising results (Kosaka et al., 2015). These oxygen carriers showed a stable activity over repeated reduction and oxidation cycles due to the absence of metal support interactions (Hossain and de Lasa, 2008).

Recently, there was increased focus on ceria as a support for oxygen carriers due to its high oxygen storage capacity with rapid formation and elimination of oxygen vacancies (Li et al., 2011). After a first reduction by hydrogen no phase transformations were found (Huang et al., 2013). In this way, the reducibility of the iron oxides is increased (Miller and Siriwardane, 2013), but after prolonged operation it is shown that a CeFeO₃ perovskite phase can accumulate leading to a deactivation of the material (Galinsky et al., 2015). By doping with La, both oxidation and reduction kinetics of CeO₂-supported iron based oxygen carriers have been improved (Bhavsar et al., 2016).

By incorporating perovskite-based mixed ionic conductors as a support into oxygen carriers its reactivity is enhanced when compared to oxygen carriers with conventional TiO₂, Al₂O₃ or YSZ supports (Galinsky et al., 2013; Protasova and Snijkers, 2016). However, some

problems are reported where interfacial diffusion of the active metal into the perovskite support results in an inhibition of the oxidation of the active metal (Shafieifarhood et al., 2015). The biggest advantage of using perovskite materials as a support is their good O²⁻ conductivity (Ismail et al., 2016). They also have the advantage of being able to accommodate significant oxygen non-stoichiometry thus allowing oxidation and reduction without phase changes. Therefore, chemically active iron-based or iron incorporated perovskite oxygen carriers with potentially improved cyclic stability are also being intensively investigated (Imanieh et al., 2016; Nandy et al., 2016; Zhao et al., 2016, 2014).

In spite of the increased interest in new supports such as ceria or perovskites, Al₂O₃ is still widely used for both CLC and CLR due to its relatively low cost, great thermal stability and the good mechanical and chemical properties of the resulting oxygen carriers. The use of air for regenerating these oxygen carriers poses no problems (Cabello et al., 2014; Zhang et al., 2014), but using steam or CO₂ might give difficulties due to the reduced oxidation kinetics of the formed FeAl₂O₄ (Najera et al., 2011). In order to inhibit the formation of FeAl₂O₄ by the solid-state reaction between the Al₂O₃ support and active Fe-oxides, the use of MgAl₂O₄ as a support has been proposed (Adanez et al., 2012). The use of MgAl₂O₄ as a support for iron based oxygen carriers results in highly reactive (Luo et al., 2014) and thermally stable (Kang et al., 2010) oxygen carriers without the aluminate formation in the reduction step because the MgAl₂O₄ spinel is more stable than the FeAl₂O₄ spinel (Leon et al., 2008). However, particle agglomeration is observed in CLC and complex phases may be formed when all four elements in these oxygen carriers interact (Johansson et al., 2004).

The development of oxygen carriers for the CLR process relies a lot on the research that has been done for the CLC process. However, due to changes in the process some oxygen carriers might react in a different way than for CLC. For example, it was observed that iron-based oxygen carriers show almost no signs of carbon deposition when utilized for CLC (Abad et al., 2007b; Cho et al., 2005). The main explanation for this is that iron oxides have several oxidation states with the higher oxidation states being more active for total combustion in CLC. When the iron oxides are being reduced more deeply (e.g. in the CLR process) the formation of Fe₃C and carbon can be observed (Svoboda et al., 2007). This is due to metals such as iron and nickel which are present in the deeply reduced OC acting as catalyst for the methane decomposition reaction into hydrogen and carbon (Galinsky et al., 2013). Despite their advantage in producing extra H₂ or CO, some problems might also occur when other oxidizing agents, such as steam and CO₂, are used for regenerating the oxygen carriers. Most frequently these problems are the result of their reduced oxidation kinetics (Najera et al., 2011) and, although frequently mentioned, this subject has not been sufficiently researched until now. Therefore this paper will address the influence of the utilization of steam for the regeneration of iron based oxygen carriers supported on Al₂O₃ or MgAl₂O₄ in a CLR process in order to determine which of these two oxygen carriers is most promising for long term use.

2. Material and methods

2.1. Materials preparation

Two types of oxygen carriers were synthesized by a spray-drying method as follows: α-Fe₂O₃ (Alfa Aesar, 98% (metals basis), –325 mesh powder), MgO (MAF Magnesite, MagChem 30) and α-Al₂O₃ (Almatis, CT3000SG) particles were dispersed in de-ionized water with the necessary dispersants (Darvan C, RT Vanderbilt, USA, or Dolapix, types A88, PC75 and PC80, Zschimmer & Schwarz, Germany). These suspensions were homogenized by milling in a planetary ball mill (Retsch, Pulverisette 5, Germany) with 3 mm Si₃N₄-balls. Afterwards, a suitable polymeric binder (polyethyleneoxide PEO, type PEO-1Z Sumitomo Seika, Japan, and/or polyvinylalcohol, PVA 15000 Fluka,

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