Hydrogen production through methane–steam cyclic redox processes with iron-based metal oxides

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ABSTRACT

The redox performance of pure iron oxide (Fe_2O_3) and iron oxide modified with ceria (CeO_2) and/or zirconia (ZrO_2) as an oxygen carrier was investigated for hydrogen (H_2) production through a methane–steam redox process. The addition of both CeO_2 and ZrO_2 were found to be a more effective modification of Fe_2O_3 than the addition CeO_2 or ZrO_2 alone. It was found that the reducibility of Fe_2O_3 was enhanced by CeO_2 and the thermal stability of Fe_2O_3 was improved by ZrO_2. These results, therefore, led to the conclusion of the synergistic effect in the Fe_2O_3-CeO_2-ZrO_2 mixed oxide. As a result, both the redox activity and the thermal stability were significantly improved, and increases in H_2 yield and purity could be maintained by the modification. The redox temperature was found to have a significant effect on redox performance. The production of H_2 was considerably improved when the redox temperature was increased from 650 to 750 °C. The ZrO_2 concentration in Fe_2O_3-CeO_2-ZrO_2 mixed oxide samples was also found to influence performance with the highest H_2 yield observed at a ZrO_2 concentration of 75 wt.%. Although all materials tested showed a reduction in surface area in the first redox cycle, the change in surface area in subsequent cycles was found to be smaller and the yield of H_2 could be maintained at a constant level over a longer period for the mixed oxide containing 75 wt.% ZrO_2.

1. Introduction

Hydrogen (H_2) is an important chemical feedstock and is also seen as an emerging energy carrier. Industrial production of H_2, however, relies on economically attractive routes from fossil fuels, including steam methane reforming (SMR). The SMR reaction is highly endothermic ($\Delta H^{\circ}_{298} = 206$ kJ/mol) and proceeds at temperatures in the range of 700–850 °C (Eq. (1)).

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (1)$$

The economic viability of the SMR is adversely affected as scale is decreased and, therefore, large scale centralised SMR is usually found to be the most cost-effective operation [1]. As the consumption of H_2 continues to increase globally, an alternative approach which offers the flexibility of utilising stranded and remote natural gas reserves is desirable for more cost-effective small scale H_2 production. As such, there is a resurgence of interest in the well-established steam–iron process. The steam–iron process is one of the few methods that require no post-reaction gas separation to produce high purity H_2 in a relatively smaller scale. The basic reactions involve a redox

loop consisting of the reduction of iron oxide with syngas (a mixture of CO and H_2) as shown in Eqs. (2a) and (2b) followed by the oxidation of the reduced iron oxide with steam (Eq. (3)).

In the reduction step:

$$Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2 \tag{2a}$$

$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O \tag{2b}$$

In the oxidation step:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \tag{3}$$

The process uses an iron/iron oxide couple as the oxygen carrier which also acts as the medium for heat transfer in repeated cycles to improve energy economics. Furthermore, a concentrated CO_x stream is obtained after condensing out the steam produced (Eqs. (2a) and (2b)). Because of these features, the interest in the steam–iron process has been extended beyond H_2 production to chemical looping combustion [2] and H_2 storage [3–5].

Although many redox couples have been considered for the looping process, the Fe_3O_4/Fe redox couple remains as one of the most preferred materials because it is inexpensive and has relatively high potential to produce high yields of hydrogen per mass of iron (48 g-H_2/kg-Fe (Eq. (3))). However, because the steam–iron process operates under repeated redox loops at high temperatures, a major challenge lies in the stabilising of the iron oxides against structural alteration via sintering or agglomeration. This irreversible physical alteration deactivates the material, decreases the lifetime and, therefore, reduces the overall process efficiency for H_2 production.

Numerous studies have been conducted in order to improve the reaction kinetics and material stability by modifying iron oxide with hetero-metals or metal oxides [6–12]. The cyclic stability of iron oxide was improved by introducing SiO_2, Al_2O_3, and $MgAl_2O_4$ as supports [9]. Otsuka et al. [6] found Al, Mo and Ce were favourable modifiers among 26 metal elements to prevent the Fe_3O_4/Fe redox activity from decaying during repeated redox cycles. In another study, the addition of Cr was found to inhibit the sintering of iron species and to improve the thermal stability of the material under the high temperatures required for reduction with CH_4 [7]. Galvita and Sundmacher [10] also reported that the activity of Cr_2O_3-doped iron oxides was sustained over 100 cycles of water–gas shift reaction. Zirconia (ZrO_2) is known to enhance structural and thermal stability [12] and Urasaki et al. [8] reported the mitigation of sintering and the improvement of oxidation in a hydrogen–steam cycle (Eqs. (2b) and (3)) when a small amount of ZrO_2 (0.23 mol.%) was added to iron oxide. Although ceria (CeO_2) sinters at elevated temperatures [11], it has good oxygen storage capacity (OSC) and has been used to facilitate many redox processes [4,13,14].

The redox process under consideration involves the reduction of iron oxides by CH_4 (Eq. (4)), followed by the oxidation with steam to produce H_2 (Eq. (5)).

$$4Fe_3O_4 + CH_4 \rightarrow 12\,FeO + CO_2 + 2H_2O \tag{4}$$

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2 \tag{5}$$
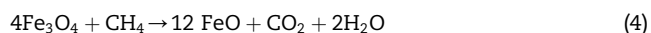
In view of the literature, the development of thermally stable and active oxygen carriers would minimise process downtime caused by material deactivation and, therefore, helps to improve the process efficiencies of the chemical looping processes. This study reports the uses of Fe_2O_3 modified with CeO_2 and/or ZrO_2 for H_2 production through a methane–steam redox looping process (Eqs. (4) and (5)) [15]. The effects of CeO_2 on redox activity and ZrO_2 on the overall thermal stability of the oxides will be discussed.

2. Experimental

2.1. Metal oxide synthesis

Oxygen carriers including pure Fe_2O_3 and Fe_2O_3 modified with CeO_2 and/or ZrO_2 were synthesised by using co-precipitation methods. Iron nitrate (MERCK, > 99%), cerium nitrate (Aldrich, 99%) and zirconium oxynitrate hydrate (Aldrich, 99%) were employed as precursors to form Fe_2O_3, CeO_2 and ZrO_2, respectively. Urea (Aldrich, 98%) was used as the precipitating agent. A number of $Fe_aCe_bZr_c$ samples were prepared with the values a, b, and c representing the loading in weight percentage of the corresponding metal oxides present in the overall structure. Previous studies indicated 60 wt.% Fe_2O_3 and 40 wt.% CeO_2 was the optimum composition to achieve rapid reduction by CH_4 [16]. This ratio was kept constant when the loading of ZrO_2 was varied. Pre-determined amounts of nitrate precursors were dissolved in distilled water and a urea solution was added before the mixture was stirred for 8 h at 90 °C. The suspension was cooled to ambient temperature. The solids were recovered, washed several times with water, dried at 80 °C and finally calcined at 500 °C in air for 3 h. All samples were ground and sieved to the desirable size of 125 −250 μm before use in order to minimise particle diffusion effects. The materials synthesised were shown by surface analysis to have very low porosity which means Knudsen style diffusion is unlikely to be a factor in these experiments.

2.2. Redox experiments

All flow rates were measured under room temperature and pressure. In all experiments, the loading of oxide was adjusted to give an equivalent Fe_2O_3 content of 85 mg. The production of H_2 from methane–steam redox cycles was investigated by using a fixed bed quartz reactor (6.0 mm I.D.) placed inside an electric furnace. Each redox cycle commenced with reduction with CH_4 (99.95%), followed by oxidation using steam. The oxide sample was first heated to a desired temperature under a flow of argon (Ar). The reduction step was commenced by introducing CH_4 to the reactor at a flow rate of 50 ml/min for 1 min. Hacker et al. [17] utilised 40–60% of the total redox potential between Fe_2O_3 and FeO. This redox potential corresponds to 10–15% of the total reducible oxygen in iron oxide and defines the reactive window in their experiments. Similarly in our study, a short reduction time was adopted in order to minimise the formation of metallic iron and, therefore, carbon formation. Then the reactor was purged thoroughly with Ar prior to steam oxidation. Steam was generated by injecting water to a flow of Ar gas (50 mL/min) in a pre-heated vessel. The final steam concentration was maintained at 57.8 vol% by controlling the amount of water injected through