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$Ca_2Fe_2O_5$: A promising oxygen carrier for CO/CH_4 conversion and almost-pure H_2 production with inherent CO_2 capture over a two-step chemical looping hydrogen generation process

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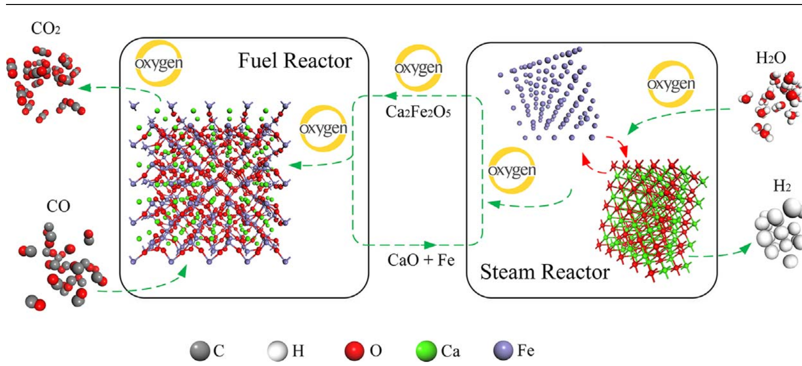
HIGHLIGHTS

- A modified sol–gel method was used for the preparation of oxygen carriers.
- A two-step chemical looping hydrogen generation process is proposed.
- The existence of Ca shows significant effect on the Fe^{3+} reduction and Fe^0 oxidation.
- The hydrogen yields could be increased by using $Ca_2Fe_2O_5$ as oxygen carrier.

GRAPHICAL ABSTRACT



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ABSTRACT

Chemical looping hydrogen generation (CLHG) is a promising technology for high-purity hydrogen production with inherent CO_2 separation. The selection of a high-performance oxygen carrier capable of being reduced and oxidized over multiple redox cycles against deactivation is a key issue for CLHG technology. In this work, a two-step chemical looping hydrogen generation (TCLHG) process is proposed by using a novel calcium ferrite, $Ca_2Fe_2O_5$, as an oxygen carrier which is synthesized with applied a citric acid assisted sol–gel method. The experimental results indicate that the reduced oxygen carrier achieves one-step oxidation from Fe^0 to Fe^{3+} by using steam as an oxidizing agent. Thus, higher yields of hydrogen could be generated compared with Fe_2O_3. The fresh and reacted Ca-Fe based oxygen carriers were characterized using different methods such as XRD, SEM/EDS, TEM, N_2 adsorption, H_2-TPR, XPS, and Mossbauer spectroscopy test etc. The oxygen release and storage capacity, cyclic stability, and carbon deposition characteristics of the Ca-Fe based oxygen carriers were investigated using TGA and a fixed bed reactor with multicycles of CO/CH_4 reduction and H_2O/O_2 oxidation. $Ca_2Fe_2O_5$ is proved to be a more stable formation of the calcium ferrite compounds and a promising oxygen carrier for TCLHG process which shows perfect reducibility, oxidation activity, and cyclic stability. The existence

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of Ca appears to perform a significant effect on the Fe^{3+} reduction and Fe^0 oxidation and the reduction from Fe^{3+} to Fe^0 was concluded to be a simple one-step reaction.

1. Introduction

Hydrogen is expected to be one of the most important energy carriers in the near future due to its increasing use in hydro-processing and hydrocracking processes and as a reduced emission fuel in combustion engines and fuel cells [1–4]. Generally, fossil fuels are used as the feedstock for hydrogen production (e.g. biomass gasification, coal gasification, and steam methane reforming). Steam-reforming of methane is currently the dominant method for large-scale H_2 production, followed by the processes of water gas shift, acid gas treatment, and pressure swing adsorption [5,6]. However, the process is complicated and the energy consumption of pressure swing adsorption is huge [7,8]. The more serious problem is a large amount of CO_2 is released into the atmosphere which aggravates the global warming. Therefore, to meet the projected demand for cheap, stable, and clean hydrogen production, an innovative hydrogen production process with a higher energy conversion efficiency, lower investment cost, and fewer environmental hazards is urgently required.

From the environmental standpoint, the chemical looping process shows the potential to capture 100% carbon from the fuels and without additional CO_2 separation steps [9,10]. Chemical looping hydrogen generation (CLHG) has been proposed as a promising technology for high-purity hydrogen production with high conversion efficiency and CO_2 separation [11,12]. The CLHG process, using iron oxide as an oxygen carrier, is generally comprised of three reactors: a fuel reactor (FR), where the carbonaceous fuel (biomass, coal, or natural gas) is oxidized to form CO_2 and H_2O; a steam reactor (SR), where the reduced oxygen carrier is oxidized by steam to produce high concentration of H_2; and an air reactor (AR), where the partially oxidized oxygen carrier is regenerated to its initial state by air [11,13,14]. The chemical reaction occurring in the CLHG process, using carbon monoxide (CO) as the fuel and ferric oxide (Fe_2O_3) as the oxygen carrier, are summarized as follows:

Fuel reactor (FR):

$$3Fe_2O_{3(s)} + CO_{(g)} \rightleftharpoons 2Fe_3O_{4(s)} + CO_{2(g)} \quad \Delta H^o_{1123\,K} = -40.8\ \text{kJ mol}^{-1} \tag{R1}$$

$$Fe_3O_{4(s)} + CO_{(g)} \rightleftharpoons 3FeO_{(s)} + CO_{2(g)} \quad \Delta H^o_{1123\,K} = 9.8\ \text{kJ mol}^{-1} \tag{R2}$$

$$FeO_{(s)} + CO_{(g)} \rightleftharpoons Fe_{(s)} + CO_{2(g)} \quad \Delta H^o_{1123\,K} = -16.5\ \text{kJ mol}^{-1} \tag{R3}$$

Steam reactor (SR):

$$3FeO_{(s)} + H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + H_{2(g)} \quad \Delta H^o_{1123\,K} = -43.4\ \text{kJ mol}^{-1} \tag{R4}$$

$$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)} \quad \Delta H^o_{1123\,K} = -94.7\ \text{kJ mol}^{-1} \tag{R5}$$

Air reactor (AR):

$$2Fe_3O_{4(s)} + 0.5O_{2(g)} \rightleftharpoons 3Fe_2O_{3(s)} \quad \Delta H^o_{1123\,K} = -237.2\ \text{kJ mol}^{-1} \tag{R6}$$

The CLHG process has many advantages: (i) inherent CO_2 separation; (ii) thermal neutrality; and (iii) reduced economic sensitivity to process scale. However, one of the major challenges of hydrogen production by chemical looping is the development of an oxygen carrier with high activity that is resistant to mechanical and chemical degradation by attrition, agglomeration, and fragmentation. When the almost pure iron oxide is used as an oxygen carrier, a rapid deactivation is found for the reduction of Fe_3O_4 to Fe within the first few cycles [15]. Limiting the extent of Fe_2O_3 reduction to FeO in every redox cycle, the cyclic stability for hydrogen production could be improved to some extent, but the transition from Fe to Fe_3O_4 produces approximately four times the hydrogen yield compared to the conversion of FeO to Fe_3O_4 [8]. Thus, the reduction from Fe_2O_3 to Fe is more conducive for hydrogen production. To improve the performances of oxygen carriers, inert supports such as Al_2O_3, $MgAl_2O_4$, ZrO_2, SiO_2, and YSZ could provide a larger surface area for reaction and act as an effective binder to increase the oxygen carrier's mechanical strength and attrition resistance [16–21]. It is also reported that incorporating iron with other elements such as Ti, La, Ce, and Sr could improve the cyclic stability of iron-based oxygen carriers and enhance the O^{2-} diffusivity [7,22–26].

More recently, Ca-Fe based catalysts have been of particular interest due to their potential in chemical looping processes [27]. Calcium ferrite is environmentally safe, chemically stable, cheap, and abundant [28]. The mixed phase of $Ca_2Fe_2O_5$ and Fe_2O_3 was used by Zamboni et al. for hydrogen production from toluene steam reforming and has been shown to contribute to the catalytic activity of Fe/CaO systems [29]. Ismail et al. prepared mixed oxides from CaO and Fe_2O_3 by using a simple mixing method and a wet impregnation method [27,30]. It has also been demonstrated that synthesized Ca-Fe based oxygen carriers have an increased capacity for hydrogen production. Martin et al. demonstrated that reduced $Ca_2Fe_2O_5$ produces more hydrogen from steam compared to unmodified Fe and a 75% conversion of steam to hydrogen was achieved with applied $Ca_2Fe_2O_5$ [31]. Kimura et al. performed in

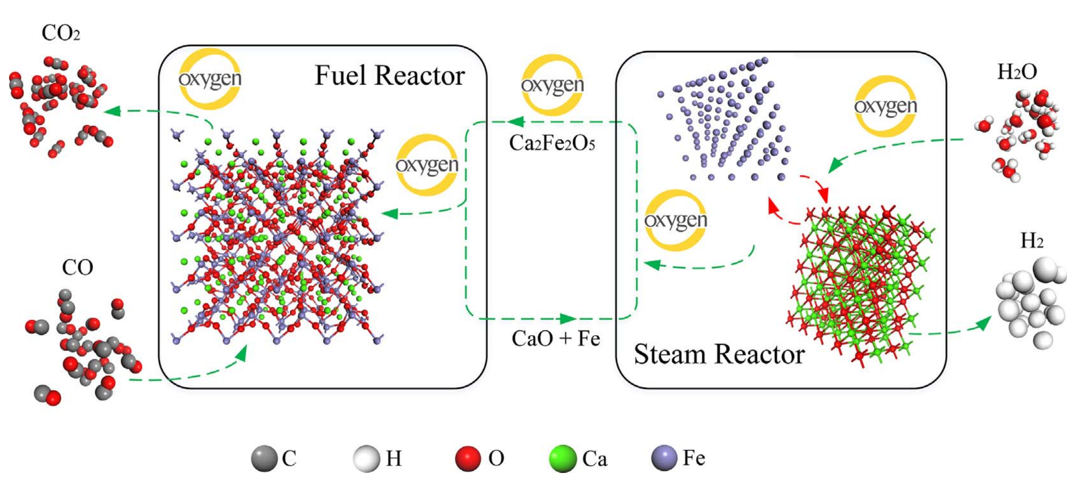

Fig. 1. Schematic of two-step chemical looping hydrogen generation (TCLHG) process using $Ca_2Fe_2O_5$ as an oxygen carrier compared with traditional chemical looping hydrogen generation process.

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