Pre-oxidation of natural ilmenite for use as an oxygen carrier in the cyclic methane–steam redox process for hydrogen production

Doki Yamaguchi [a],*, Liangguang Tang [a], Ken Chiang [b]

[a] CSIRO Energy, Private Bag 10, Clayton South, VIC 3168, Australia
[b] School of Engineering, RMIT University, Melbourne, VIC 3000, Australia

HIGHLIGHTS

- Pre-oxidation influenced morphology and crystallinity of ilmenite.
- Fe_2TiO_5 formation promoted oxygen transfer capacity.
- Three-fourfold increase of H_2 production when ilmenite was pre-oxidised at 1000 °C.

ARTICLE INFO

ABSTRACT

The methane–steam redox process is an alternative methane conversion route to high-purity hydrogen production. Using natural ilmenite as an oxygen carrier, we investigated the effect of three different pre-oxidation temperatures (800, 1000 and 1200 °C) on redox performance and stability. We found that the pre-oxidation temperature significantly altered the crystalline properties of the ilmenite sample, which subsequently affected its morphology, reducibility and redox performance. Pre-oxidation above 1000 °C caused the formation of pseudo-brookite (Fe_2TiO_5), while hematite (Fe_2O_3) was formed at 800 °C. The presence of Fe_2TiO_5 lowered the reduction kinetics, but improved the oxygen-transfer capacity. This resulted in the highest redox activity for the sample pre-oxidised at 1000 °C, which had a three to fourfold increase in hydrogen yield compared with samples pre-oxidised at the other temperatures. Redox activity progressively increased during the cyclic redox operation, due to an increase in surface area caused by continual pore and crack development. Hydrogen yield was sustained at double the level of the initial yield, with a purity of more than 98% over 40 redox cycles.

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1. Introduction

Methane is the main component of natural gas. The conversion of methane into hydrogen is a vital process supporting current industrial activities in the metallurgy, chemical, petroleum, pharmaceutical and food sectors. Considering the shortfall in hydrogen caused by increasing global demand for electricity generation and transportation, the production of hydrogen from methane will continue to be important. The projected increase in natural gas prices, combined with the need for lower-emission technologies, means that more efficient, cost-effective techniques to convert both conventional and unconventional natural gas resources will be required [1].

The methane–steam redox process, also known as chemical-looping process, is an alternative route for producing high-purity hydrogen from methane. It is based on the well-established steam-iron process, which was first validated in the late 18th century and has been further studied by several groups [2–6]. As the source of oxygen, the steam-iron process and its derivatives use the lattice oxygen in metal oxide (e.g. Fe_3O_4). Once the available oxygen in the metal oxide is depleted, the oxygen content in its reduced state can be enriched by oxidation. Because of the redox capacity of many metal/metal-oxide couples, these materials are often referred to as oxygen carriers.

Ideally, the cyclic redox process generally consists of two reactors: one for reduction and one for oxidation. For the methane–steam redox process of interest to this study, hydrogen is produced by first reacting methane with a metal oxide (Me_xO_y) (Eq. (1)), followed by oxidation of the reduced metal oxide (Me_xO_{y-1}) with steam (Eq. (2)).
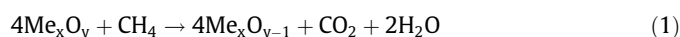
$$4Me_xO_y + CH_4 \rightarrow 4Me_xO_{y-1} + CO_2 + 2H_2O \tag{1}$$

$$Me_xO_{y-1} + H_2O \rightarrow Me_xO_y + H_2 \qquad (2)$$

To produce high-purity hydrogen, commercial hydrogen production processes, such as steam reforming, generally require post-treatment processes. These can include two-stage water-gas shift reaction, methanation, and gas separation for high-purity hydrogen production. The methane–steam redox process scheme could simplify the production process by eliminating these post-reaction separation processes. During methane oxidation, steam is condensed into water, with concentrated carbon dioxide produced as a result (Eq. (1)). Therefore, hydrogen can be produced with minimal contamination, because it is the only gas formed in the oxidation reaction (Eq. (2)). The metal oxide acts as a heat-carrying medium, and improves the overall energy efficiency and process economics. The process is more efficient in smaller-scale operations that favour a distributed supply of hydrogen.

By controlling the operating conditions of the methane–steam cycle, the production of syngas (a mixture of H_2 and CO) can be maximised (Eq. (3)). This is an important building block for the production of many synthetic fuels and chemicals [7–9].

$$Me_xO_y + CH_4 \rightarrow Me_xO_{y-1} + CO + 2H_2 \qquad (3)$$
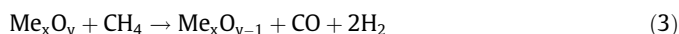
The overall process efficiency and economics of the methane–steam process are determined by the chosen oxygen carrier's redox activity and lifetime. Iron-based oxides have been preferred as oxygen carriers because they are abundant, inexpensive and environmentally friendly. They also have a higher oxygen storage capacity than other transitional metal oxides, and therefore contribute to more efficient conversion per unit metal-mass. However, the thermal stability of iron oxides, particularly at temperatures >700 °C, requires improvement. At such high temperatures, they undergo significant structural alternation via irreversible sintering, which leads to irreversible deactivation [3,6,10]. To improve their thermal stability, iron oxides are often modified with dopants or metal oxides. In a previous study [6], we modified iron oxide with ceria and zirconia. This significantly improved material stability, lifetime and reaction rate, allowing us to produce high-purity hydrogen over a repeated methane–steam redox operation. Galvita et al. [11] studied a similar material (iron oxide modified with ceria and zirconia), and revealed significant suppression of sintering and constant activity over 100 cycles of the water-gas shift reaction. Chromia [2,12] and titania [13,14] have also been suggested as candidates to improve iron oxide stability.

Inexpensive, natural iron-containing minerals are possible alternatives to synthetic iron oxide materials for use in the methane–steam redox process. Minerals such as iron ores [15–17], oxide scales [15,16] and ilmenite (mainly composed of $FeTiO_3$) [16,18–21] have all been tested as oxygen carriers for chemical-looping combustion. Various feedstocks, including methane, syngas and solid fuels (petroleum coke and coal) were used as reducing agents in these studies, and the reduced oxide material was subsequently oxidised with air or diluted oxygen. Leion et al. found ilmenite to be a promising oxygen carrier [16], because of its high redox activity, high stability against sintering and agglomeration, low cost, environmentally benign nature and high mechanical strength against attrition [18,22,23]. In addition to its chemical-looping combustion applications, the effects of oxidative treatment on the properties of ilmenite (e.g. reduction/oxidation kinetics, crystallinity, morphology) during the production of titanium dioxide pigment have been investigated [24–28]. A more specific, detailed study of ilmenite properties during chemical-looping combustion cycles was conducted by Adanez et al. [20].

In this work, we report the use of natural ilmenite as an oxygen carrier in the methane–steam redox process for the production of hydrogen. We discuss the changes in the redox performance caused by pre-oxidation, as well as the redox operation via charac-

terisation of samples before and after consecutive methane–steam redox cycles conducted in a fixed-bed reactor.

2. Experimental

2.1. Ilmenite sample

The oxygen carrier employed in this study is a natural ilmenite, which mainly consists of a mixture of titanium and iron oxides ($FeTiO_3$). The ilmenite samples were used as received (denoted as 'raw') or were pre-oxidised at 800, 1000 or 1200 °C in a muffle furnace for 2 h (hereafter denoted as Cal800, Cal1000 and Cal1200). The chemical composition of the samples was determined by X-ray fluorescence (XRF) and ferrous iron [Fe(II)] analysis. For Fe(II) content determination, ilmenite samples were digested by hydrofluoric acid and then titrated with a $K_2Cr_2O_4$ solution.

2.2. Materials characterisation

The specific surface area of each sample was determined from nitrogen adsorption using a Micromeritics TriStar 3000. Before measurement, the samples were degassed overnight at 300 °C.

The X-ray diffraction (XRD) analysis was carried out on a Phillips DW 1130 XRD, equipped with a radiation source of Cu Kα ($\lambda = 1.5406$ Å) and operated at 40 kV and 25 mA. The diffractograms were recorded in a 2θ range from 10 to 80° with a step size of 0.05° and a scanning speed of 1°/min. A scanning electron microscope (SEM; ZEISS, SUPRA™ VP40) was used to investigate morphological properties of the ilmenite samples. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Thermo Scientific ESCALAB250Xi with a mono-chromated Al Kα (energy 1486.68 eV) X-ray source.

Temperature-programmed reduction (TPR) analysis was carried out in a Mettler-Toledo TGA/SDT851 thermogravimetric analyser. Each sample was first dried at 150 °C under a nitrogen environment before it was reduced in a flow of diluted hydrogen (4% H_2/ N_2). The temperature was ramped up from 150 to 950 °C at a heating rate of 5 °C/min. When the terminal temperature of 950 °C was reached, the sample was held at this temperature for 90 min. The corresponding differential thermogravimetric (DTG) analysis was obtained from the first derivative of the weight loss curve of the samples and was used to analyse the reduction profile of the samples. The O/Fe molar ratio was used to indicate the valance state or reduction degree of iron oxide in the ilmenite samples. It was calculated by dividing the cumulative mole of oxygen reduced during the TPR analysis by the total mole of iron contained in the sample. For example, the O/Fe ratio = 0.0 represents the ilmenite samples in the maximum oxidising state (e.g. Fe_2O_3 or Fe_2TiO_5) whereas the O/Fe ratio = 1.5 indicates the maximum reduced state (Fe^0).

The oxygen-transfer capacity of samples was determined from cyclic methane-oxygen redox experiments, which were conducted isothermally at 850 °C in the TGA. In a typical analysis, 20 mg of a sample was loaded into an alumina crucible and heated to 850 °C in a flow of argon. When a stable weight was reached, the sample was reduced in a flow of 30% CH_4 in argon for 20 min followed by oxidation in 20% O_2/Ar for 2 min. Argon was purged through the sample chamber to remove any residual CH_4 or O_2 in the system after each step of reduction or oxidation. The obtained weight loss curves were normalised and used to evaluate the oxygen-transfer capacities of samples.

2.3. Methane–steam redox experiments

Methane–steam redox experiments were conducted isothermally at 800 °C in a fixed-bed quartz reactor with an internal diam-