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CeO₂ modified Fe₂O₃ for the chemical hydrogen storage and production via cyclic water splitting

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ABSTRACT

The chemical hydrogen storage (hydrogen reduction) and production (water splitting) behaviour of Ce-modified Fe₂O₃ mixed oxides were investigated. Fe_{1-x}Ce_xO_{2-δ} (x = 0, 0.05, 0.1, 0.2, 0.3, 0.4 and 1) oxides prepared by chemical precipitation were characterized by XRD (X-ray diffraction), H₂-TPR (hydrogen temperature-programmed reduction) and H₂O-TPO (steam temperature-programmed oxidation) tests. XRD results showed that two kinds of Fe–Ce–O solid solutions (Ce-based and Fe-based) coexisted in Fe–Ce mixed oxides. H₂-TPR experiment suggested that Ce addition could reduce hydrogen reduction temperature while H₂O-TPO experiments over reduced oxides showed that Fe–Ce mixed oxides could split water to produce hydrogen at a lower temperature and complete in a shorter time. Both redox reactions (hydrogen reduction and water splitting) were sensitive to the temperature and active at a high temperature. The successive redox cycles were carried out over the Fe_{0.7}Ce_{0.3}O_{2-δ} mixed oxide at 750 °C. It kept a stable production of hydrogen in the successive redox process at the condition of serious agglomeration of the materials. The highest hydrogen storage amount was up to 1.51 wt% for the Fe–Ce sample with a 30% substitution of Ce for Fe.

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Introduction

Hydrogen is deemed as an environmentally energy source and clean energy carrier in the future [1]. The hydrogen production, storage, transportation and utilization are being performed to solve the hydrogen energy application [1,2]. The compressed gas storage is the recent dominant technology for

the hydrogen storage. But its efficiency is still low because of low energy density and safety issues. Liquid hydrogen is available in modern liquid-hydrogen plant. Its hydrogen storage capacity is about 5 wt%. However, liquefaction process for hydrogen needs to consume large quantities energy besides issues involved in storage vessel and safety. Currently, many researchers have been paid attention to metal hydrides, chemical hydrides and physical adsorption [3,4].

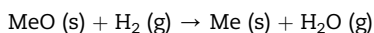
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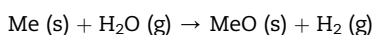
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An unconventional chemical hydrogen storage method was proposed by Otsuka et al. based on the redox of metal oxides [5–11]. This process consists of hydrogen reduction and water splitting steps.

Step 1: hydrogen storage (hydrogen reduction):



Step 2: hydrogen production (water splitting):



Through recycled step 1 and step 2, hydrogen can be stored and then produced as required. Iron oxide was the common materials used in this process because that it is cheap and reactive with relative low molar weight [12]. Some drawbacks involved in this Fe-based chemical hydrogen storage and production system. Single Fe_2O_3 or Fe_3O_4 was likely to sintering during the high-temperature redox process. Besides, the reaction temperature for the hydrogen reduction of Fe oxides and water splitting over reduced Fe species still remained high, which will consume energy and reduce its economy [10].

In our previous study, we found that in combination of Ce and Fe oxides will greatly promote their reducibility and redox activity [13–16]. Chemical interaction between Ce and Fe species in Fe–Ce mixed oxides has been observed in chemical-looping steam methane reforming, and proved to be favourable for the hydrogen production in water splitting step. Therefore, CeO_2 modified Fe_2O_3 was investigated in chemical hydrogen production on the basis of our previous research.

In this work, a series of Fe–Ce oxides prepared by chemical precipitation was studied in steam (H_2O) temperature-programmed oxidation (H_2O -TPO) experiments to obtain the effect of Ce addition and reaction temperature. Selected Fe–Ce mixed oxides was submitted to successive redox cycles to study the durability for the chemical hydrogen production.

Experimental

Materials preparation

$\text{Fe}_{1-x}\text{Ce}_x\text{O}_{2-\delta}$ ($x = 0, 0.05, 0.1, 0.2, 0.3, 0.4$ and 1) oxides were prepared by chemical precipitation. $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and/or $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were mixed according to the mole ratio to produce a solution at room temperature. Ammonia was introduced to salt solution to precipitate cation with stirring. When the pH value was increased to 9–10, the resulting mixture was continued to stir for 3 h. The resulting precipitate was filtered and washed with distilled water and ethanol after

settling for 1 h. The precipitate was then submitted to dry at 110°C for 24 h to produce a massive object. The object was calcined at 300°C for 5 h and 500°C for 10 h under ambient air and crushed to a powder. This powdery sample was pressed under 10 MPa for 10 min to produce granules with a 20–40 mesh size.

Materials characterization

Powder X-ray diffraction (XRD) patterns were recording using a Japan Science D/max-R diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) at 40 kV and 40 mA in the 2θ range between 10° and 80° .

Hydrogen temperature-programmed reduction (H_2 -TPR) patterns were recorded using a TPR Win v 1.50 (produced by Quantachrome Instruments Co.). The sample (100 mg) was heated from 100 to 900°C in a $75 \text{ cm}^3/\text{min}$ flow of 10% H_2/He at a heating rate of $10^\circ\text{C}/\text{min}$. The consumption of H_2 was recorded by TCD (thermal conductivity detector).

Scanning electron microscopy (SEM) was performed on a Philip XL30 instruments using accelerating voltages of 30 kV. Samples for SEM were dusted on an adhesive conductive carbon belt attached to a copper disk prior to measurement.

Experimental set-up

Steam (H_2O) temperature-programmed oxidation (H_2O -TPO) experiments were performed on a fixed-bed reactor under a steam (H_2O) flow rate of $0.1 \text{ cm}^3/\text{min}$ with N_2 carrier gas ($200 \text{ cm}^3/\text{min}$) over 250 mg sample using a heating rate of $10^\circ\text{C}/\text{min}$ in the range between 200 and 750°C . Prior to H_2O -TPO test, the sample was dried in N_2 at 100°C for 0.5 h, and then reduced in a flow of 10% H_2/N_2 mixture ($200 \text{ cm}^3/\text{min}$) from 100 to 550°C at a heating rate of $10^\circ\text{C}/\text{min}$ and at 550°C for 1.5 h. The evolved gas from fixed-bed reactor was analysed by on-line hydrogen detector (QRD-1102C, by Beijing BAIF-Maihak Analytical Instrument Co., Ltd.) after condensation and purification. The steam was generated by injecting demineralized water using a micro pump (P230, Dalian Elite Analytical Instruments Co., Ltd.).

For the isothermal water splitting reaction, gas–solid reaction between steam and sample was carried out in a fixed-bed reactor under atmospheric pressure. An amount of 1.0 g of sample was placed in a quartz tube with 20 mm inside diameter. Prior to water splitting reaction, the sample was dried in N_2 at 100°C for 0.5 h, and then pure H_2 was flowed to the reactor at desired temperature for 30 min. The water splitting reaction was initiated by passing steam with N_2 carrier gas ($50 \text{ cm}^3/\text{min}$) through the reactor for 15 min. The evolved gas at different reactions was detected by gas chromatograph (Agilent 7890A GC System, produced by Agilent Co.) which is equipped with HP-Plot 5A and HP-Plot-Q column.

Successive redox cycles: after the reduction reaction between H_2 ($50 \text{ cm}^3/\text{min}$) and the metal oxide (1 g) had proceeded for 30 min (hydrogen reduction), steam was introduced at a flow rate of $0.1 \text{ cm}^3/\text{min}$ with N_2 carrier gas ($50 \text{ cm}^3/\text{min}$) for 30 min to regenerate the reduced sample (water splitting). These sequences were separated by a purge with pure N_2 ($200 \text{ cm}^3/\text{min}$) for 15 min, to avoid mixing the

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