Synthesis of Nano-Sized Ferrite Materials for H_2 Generation from High Temperature Water-Splitting Reaction

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ABSTRACT

This paper reports the synthesis of Ni-ferrite nanorods by an inorganic condensation method using PEG surfactant templating for H_2 generation from water-splitting reaction. In this synthesis, salts of Ni and Fe, NaOH and PEG-400 were mixed in 1:0.6:1.2 (w/w) ratio and ground with a pestle and mortar, which resulted into a black colored paste. This paste was washed twice thoroughly using deionized water and subsequently with 95% ethanol to remove PEG-400 surfactant and the solids were dried and calcined at 600°C in air. The calcined powder was characterized using powder x-ray diffraction, BET surface area analyzer, scanning and transmission electron microscopy. As-synthesized Ni-ferrite nanorods were then used to investigate H_2 generation from thermochemical water-splitting reaction at 800°C.

Keywords: Ni-ferrite nanorods, inorganic condensation, H_2 generation, metal oxide, thermochemical water-splitting.

1 INTRODUCTION

With the search for alternative energy carriers and with H_2 as a potential option for the future, the research to find sustainable routes of H_2 production has intensified [1]. Thermal decomposition of water yielding pure H_2 is considered to be the most attractive reaction for the production of H_2 [2]. Among several water-splitting processes available for H_2 generation, a metal oxide (MO)-based thermochemical water-splitting process has been regarded as the simplest, as well as most environmentally benign [3]. It is a two-step process, which utilizes redox reactions of mixed valence metal oxides [4]. In the first step (1), the reduced MO is oxidized by taking O_2 from water and producing H_2 via water-splitting (W-S) reaction [5]:

$$MO_{reduced} + H_2O \longrightarrow MO_{oxidized} + H_2\,(g) \qquad (1)$$

In the second step (2), the oxidized MO is converted back to its reduced form by releasing O_2 during thermal reduction (T-R) step [5]:

$$MO_{oxidized} \longrightarrow MO_{reduced} + \tfrac{1}{2}\,O_2\,(g) \qquad (2)$$

The T-R step typically requires higher temperatures as compared to the W-S step. The combination of one T-R step and one W-S step can be termed as one thermochemical cycle [6].

Phase pure ferrites such as $NiFe_2O_4$ [7], $ZnFe_2O_4$ [8], $MnFe_2O_4$ [9] and doped ferrites, for instance, $Ni_xMn_yFe_2O_4$ [10], $Ni_xZn_yFe_2O_4$ [11] and $Zn_xMn_yFe_2O_4$ [9] were reported to be the most reactive materials available for H_2 generation from thermochemical water-splitting reaction. Most of these ferrites have been synthesized by solid-state mixing (SSS), oxidation of aqueous metal hydroxide suspension, self-propagation high temperature synthesis (SHS), aerosol-spray pyrolysis (ASP) or sol-gel technique [2-3, 5-6, 12-14]. Recently, we have reported H_2 generation from thermochemical water-splitting using Ni-ferrite [13], Zn-ferrite [12], Mn-ferrite [14] and Zn/Mn/Sn-doped Ni-ferrite [2] synthesized by sol-gel technique.

Among the above listed ferrites investigated so far, Ni-ferrite was reported to be the most promising material for H_2 production. In our previous investigations, we reported that the Ni-ferrite synthesized using the sol-gel technique produced 7 mL/g per cycle of H_2 in four consecutive thermochemical cycles, where W-S was performed at 700°C and T-R was carried out at 900°C [13], which is the lowest regeneration temperature reported in the case of Ni-ferrite so far. Similarly, Ni-Zn-ferrite and Ni-Mn-ferrite generated an average of 4.65 and 3.72 mL/g per cycle of H_2 in multiple thermochemical cycles where W-S and T-R steps were performed at 800°C and 1100°C, respectively [2]. The volume of H_2 generated by these sol-gel derived ferrites is higher as compared with the H_2 generated by similar ferrites synthesized using different synthesis approaches such as SHS, SSS etc.

The ferrites synthesized by the sol-gel technique yields nanoparticles with high specific surface area (SSA) ranging from 30 – 40 m^2/g after calcination at 600°C in air [2-3, 5-6, 12-14]. Because of the porous/nanoparticle morphology, there is a possibility that the diffusional limitations and mass-transfer resistances involved during the W-S and T-R steps may be eleminated. In addition to this, the higher SSA may provide higher number of active sites for W-S reactions resulting in higher levels of H_2 production. Therefore, we believe that, as the current research trends are focused towards lowering the W-S and T-R temperatures, the ferrites with porous/nanoparticle morphology are preferabel to reduce the H_2 generation temperatures. In addition to the ferrite nanoparticles, it will be interesting to investigate one-dimensional ferrites, nanorods, for their application towards H_2 generation via W-S reaction. Although, a vast knowledge

is available on the synthesis of ferrite nanorods by various methods [15-20], their application for H_2 generation using thermochemical W-S reaction has not yet been reported.

In this paper, we report synthesis of Ni-ferrite nanorods by an inorganic condensation method using PEG surfactant templating [21] and its characterization using powder X-ray diffraction, BET surface area analyzer, scanning (SEM) and transmission electron microscopy (TEM). Ferrite nanorods were then used to investigate H_2 production from W-S reaction at 800°C.

2 EXPERIMENTAL

2.1 Synthesis of Ni-Ferrite Nanorods

Ni-ferrite nanorods were synthesized by an inorganic condensation method using a PEG surfactant. In this method, $NiCl_2 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ (1:2 w/w), NaOH and PEG-400 were mixed together in the weight ratio of 1:0.6:1.2 and ground with a pestle and mortar. Mixing and grinding was continued for 30 min, which resulted in a black colored paste. This paste was sonicated with 500 mL of deionized water using sonic wand for 3 h and then kept overnight undisturbed that allowed the solids settle down. Further, the solids were washed thoroughly with ethanol and deionized water to remove the surfactant and other impurities and then centrifuged at 4000 rpm for 10 min. The solids were dried at 100°C for 2 h, pulverized and then calcined slowly (heating rate of 1°C/min) upto 600°C and soaked at this temperature for 4 h in air.

2.2 Characterization of Ni-ferrite Nanorods

The Ni-ferrite nanorods obtained after the calcination were analyzed for compositional purity by Rigaku Ultima-Plus X-ray diffractometer (XRD) ($10^o \leq 2\theta \leq 70^o$ and scanning speed of 2^o per minute). The morphology of the calcined powder was analyzed using Zeiss Supra 40 VP field-emission scanning electron microscope (SEM) and Hitachi H-7000 FA transmission electron microscope (TEM). BET surface area analyzer, Gemini II-2375 from Micromeritics, was used to determine the SSA of the calcined powder from the adsorption isotherm obtained after degassing the material at 200°C.

2.3 Hydrogen generation set-up

The H_2 generation ability of the Ni-ferrite nanorods synthesized by an inorganic condensation method via PEG surfactant templating was investigated using thermochemical water-splitting reactor set-up shown in Figure 1. It consists of a tubular packed bed Inconel reactor enclosed in a vertical split furnace (Carbolite Inc., USA). The temperature of the furnace was controlled and regulated precisely with the in-built PID controller. Accurately weighed 5.0 g of the Ni-ferrite nanorods were packed in the middle section of the tubular reactor with the

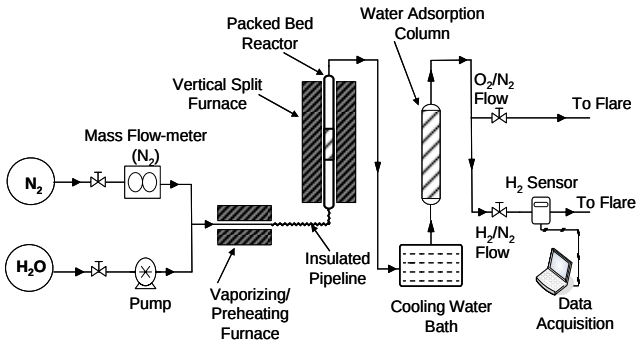

Figure 1: Thermochemical water-splitting reactor set-up for H_2 generation [14].

help of Raschig rings and quartz wool. A horizontal tube furnace was provided with a stainless steel tube and it was used as a water vaporizing/preheating set-up. Distilled water from the reservoir was fed to the vaporizing/preheating furnace using a metering pump (Fluid Metering Inc., USA) at the flow rate of 1 mL/min. Water vaporized and the preheated steam obtained was fed to the packed bed reactor with N_2 as a carrier gas. A mass flow meter for N_2 (AALBORG Inc., USA) was mounted on the feed line to control the gas flow rate; a flow rate of about 100 mL/min was randomly selected. The exit gas stream from the packed bed reactor was first cooled down in a water bath and finally fed to the moisture adsorption column containing anhydrous calcium sulfate purchased from W.A. Hammond Drierite Company Inc., OH, USA. The exit gas stream (mixture of N_2 and H_2) from the adsorption column was continuously monitored using an online H_2 sensor. The sensor provided H_2 concentration in vol% at an interval of 1 sec. The effluent gas stream was burned continuously. The water supply was continued until the online H_2 sensor indicated 0.0 (vol%) concentration level. Using this experimental set-up, the W-S and T-R ability of Ni-ferrite nanorods was investigated by performing multiple thermochemical cycles at W-S and T-R temperatures of 800°C and 1000°C, respectively.

3 RESULTS AND DISCUSSION

Ni-ferrite nanorods were synthesized as per the procedure described in Section 2.1. The reaction of $NiCl_2 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$ and NaOH was moderately exothermic in nature. Addition of PEG in this mixture helps in confining the growth in a nanoscale [21] and provided template for the growth of Ni-ferrite nanorods. After grinding the mixture, the surfactant and other impurities from the solids were removed by repeatable washing using deionized water and ethanol. The solids obtained after centrifugation were heated slowly in a muffle furnace upto 600°C and soaked at this temperature for 4 h in air atmosphere. The compositional purity of the calcined powder was determined using the powder x-ray diffraction and the XRD pattern obtained is shown in Figure 2. The 2θ reflections of 18.2, 30.1, 35.5, 37.2, 43.2, 53.7, 57.2, 62.8 and 66.1 match with standard international Catalogue for

Diffraction Data (ICDD) pattern of $NiFe_2O_4$ (Trevorite), which indicates that the calcined powder is nominally phase pure Ni-ferrite. This XRD pattern and reflections are also consistent with those reported by our group elsewhere [13].

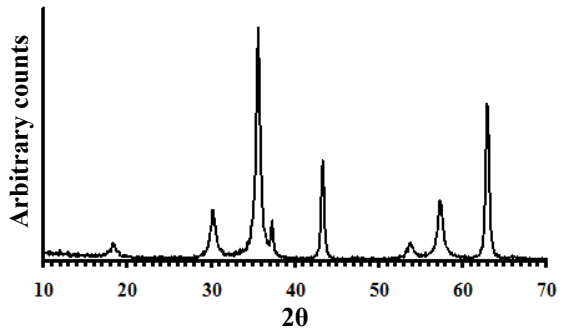

Figure 2: XRD pattern of $NiFe_2O_4$ (Trevorite) powder calcined at 600°C for 4 h in air.

The morphology of the calcined Ni-ferrite powder was studied using SEM and TEM. The SEM image shown in Figure 3a indicated smaller grains with average particle size in the range of 100 - 300 nm. Further, the morphology of the calcined powder was analyzed using TEM and the image obtained (shown in Figure 3b) indicated that the Ni-ferrite nanocrystals have a rod-like geometry with the aspect ratio of about 3 – 10.

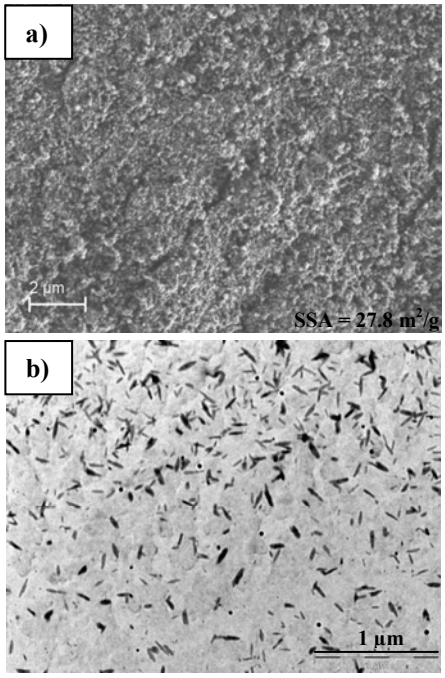

Figure 3: a) SEM and b) TEM images of $NiFe_2O_4$ nanorods calcined at 600°C for 4 h in air.

The H_2 generation ability of Ni-ferrite nanorods, was investigated by performing three thermochemical cycles where W-S and T-R steps were performed at 800°C and 1000°C, respectively. Accurately weighed 5.0 g of the Ni-ferrite nanorods were placed in an Inconel tubular reactor and heated to W-S temperature of 800°C. The 1st water-splitting step was performed without T-R step as this can cause potential grain growth and decrease SSA. After reaching the W-S temperature, the preheated steam from the vaporizing/ preheating set-up at 500°C was fed to the rector. The H_2 evolution was recorded continuously using the online H_2 analyzer. After W-S step, the material was regenerated at 1000°C for 3 h in N_2 environment and the reactor was again cooled down to 800°C to perform subsequent W-S cycles. Three consecutive thermochemical cycles were performed and the transient H_2 profiles obtained are shown in Figure. 4.

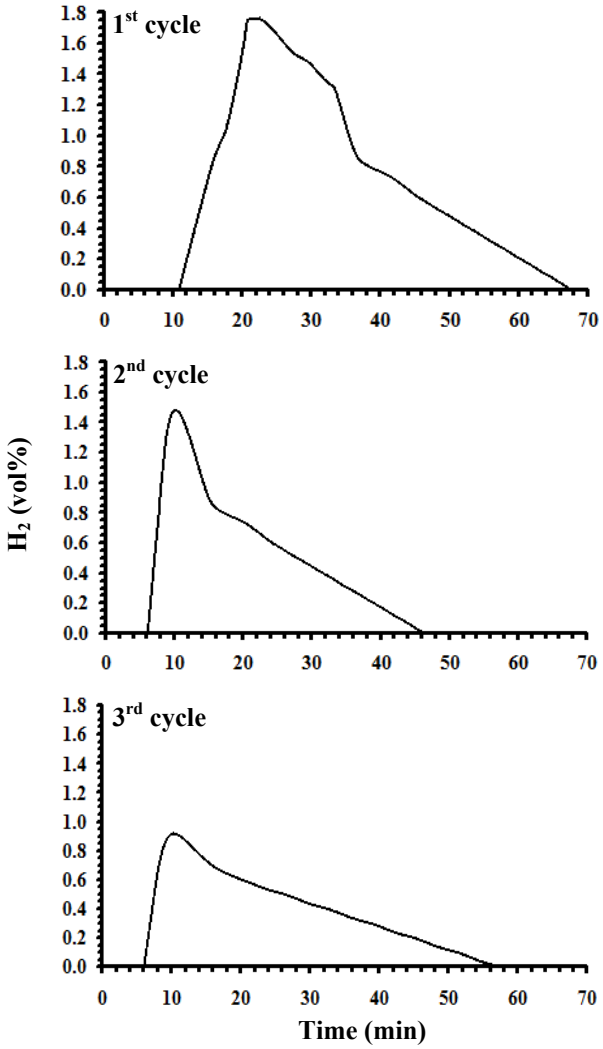

Figure 4: Transient H_2 profiles obtained during three thermochemical cycles where W-S was performed at 800°C using Ni-ferrite nanorods.

From the obtained results, it was realized that the Ni-ferrite nanorods synthesized here are capable of producing H_2 via thermochemical water-splitting reaction at lower W-S and T-R temperatures. However, it was also observed that the vol% of H_2 generated decrease in subsequent W-S steps. The possible reason for this decrease in H_2 production during subsequent W-S steps may be attributed to the poor regeneration ability of these ferrites at 1000°C. In addition to this, the decrease in SSA and grain growth or sintering of the ferrites due the continuous and cyclic exposure to the higher temperatures for several hours, might be another reason for the decrease in vol% of H_2 during multiple thermochemical cycles. Further efforts are in progress towards verifying this hypothesis and to quantify the ability of H_2 generation.

4 CONCLUSIONS

Ni-ferrite nanorods were successfully synthesized by an inorganic condensation method using PEG surfactant templating method followed by calcination at 600°C in air environment. The XRD analysis revealed a phase pure composition of $NiFe_2O_4$ (Trevorite). Further, the characterization of calcined powder via TEM indicated nanorods with the aspect ratio of about 3 – 10. As-synthesized Ni-ferrite nanorods were used for H_2 production in three consecutive thermochemical cycles where W-S step was performed at 800°C and the T-R step was carried at 1000°C, respectively. In three consecutive thermochemical cycles, the Ni-ferrite nanorods produced significant vol% H_2 from 5.0 g of ferrite material loaded in the packed bed reactor. However, after each W-S step, a decrease in the H_2 production level was observed.

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