**Evaluation of nanoparticle zirconia supports in the
thermochemical water splitting cycle over iron oxides**

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Abstract

Two-step solar thermochemical water splitting offers a viable solution for employing renewable energy pathways for production of high-purity hydrogen, which can be used in fuel cells or for the production of liquid fuels. One promising thermochemical cycle uses iron oxide as the reactive material to split water in a relatively simple two-step process. However, this cycle requires high temperatures, on the order of 1,500 °C. Therefore, in order to increase stability and thermal shock resistance, iron oxide was deposited onto high-temperature-stable ceramic oxides, such as zirconia (ZrO_2) and yttria-stabilized zirconia (YSZ). Nanoparticle zirconia samples (n- ZrO_2 and n-YSZ) were used in this study to increase the interactions between the iron oxide and the zirconia, and the resulting materials were compared with an iron oxide supported on a commercially available porous zirconia support (p- ZrO_2). After heat treatment, these $\text{FeO}_x/\text{n-ZrO}_2$ and $\text{FeO}_x/\text{n-YSZ}$ materials were surprisingly stable and yielded consistent hydrogen production over several cycles. The hydrogen yield per cycle for the $\text{FeO}_x/\text{n-YSZ}$ material was consistently higher for all iron loadings compared with the $\text{FeO}_x/\text{n-ZrO}_2$ materials, and they both yielded significantly more hydrogen compared to the FeO_x supported on the commercial ZrO_2 support. Compared with the $\text{FeO}_x/\text{n-YSZ}$, the iron loading had a larger effect on the hydrogen production over n- ZrO_2 -supported materials. X-ray diffraction (XRD) data indicated that iron was incorporated into the unit cell lattice of the n-YSZ supported material, which alleviated some of the detrimental iron oxide sintering inherent at the high-temperatures of the thermochemical water splitting reaction, and resulted in a more consistent and higher hydrogen production compared with the $\text{FeO}_x/\text{n-ZrO}_2$ material.

Keywords: Thermochemical water-splitting; hydrogen production; iron oxide; zirconia nanoparticles; X-ray diffraction (XRD)

1. Introduction

The production of clean, transportable, and renewable fuels is needed to reduce our dependence on fossil fuels. According to the United States Energy Information Administration, global consumption of liquid fuels averaged 92.1 million barrels per day (bbl/d) in 2014 and is expected to grow by 1.0 million bbl/d in 2015 and 2016 [1]. Fossil fuels, such as petroleum oil, natural gas, and coal, are the current major energy sources; however, the limited supply as well as the pollutants and greenhouse gases produced by these fuels motivate the need for a green alternative. Clean processes are available that utilize hydrogen (H_2) as an energy transfer medium. The benefit of using hydrogen as an energy carrier is that the byproduct from internal combustion is water, making it a non-polluting process [2-4]. Furthermore, if hydrogen is produced from renewable energy sources such as solar energy, this becomes a sustainable clean energy solution.

Hydrogen is an attractive energy carrier as it has been effectively used in internal combustion vehicles and polymer electrolyte membrane (PEM) fuel cells [2,5,6]. H_2 as a gas can also be successfully transported over long distances via pipelines at the same cost as electricity [7] and can be generated from a number of pathways and resources. Solar energy is one of the largest renewable resources and can provide the energy required to drive the decomposition of water into its constituent parts, H_2 and oxygen (O_2), in a thermochemical cycle [8,9]. Development of efficient thermochemical processes that utilize solar energy to produce H_2 is therefore highly desirable.

Hydrogen production via direct water splitting is highly endothermic, thermodynamically unfavorable, and results in H_2 and O_2 separation issues. Furthermore, prohibitively high temperatures, exceeding 4,000 °C, are needed for direct water dissociation to establish a

favorable Gibb's free energy [10-13]. An alternate route, which aids in lowering the operating temperatures significantly, is to use solar thermochemical reactions that involve simple chemical reactions with relatively few steps. Two-step metal oxide cycles are promising in thermochemical water splitting [14]. One metal oxide pair that has successfully produced H₂ is Fe₃O₄/FeO, as originally proposed by Nakamura in 1977 [15]. The two-step reaction for iron oxide water splitting is as follows:

In the water splitting (WS) step, an oxygen-deficient iron oxide (FeO) reacts with steam to form Fe₃O₄ and hydrogen is released. This step is slightly exothermic and becomes thermodynamically favorable at approximately 800°C, which is a much lower temperature than direct water splitting. In the second step, the iron oxide from the WS step is heated until oxygen desorbs (is released) and the oxygen-deficient iron oxide is regenerated. This step is highly endothermic and requires temperatures in excess of 1,500 °C. Additionally, an inert gas is flown over the material during the thermal reduction (regeneration) step to reduce the partial pressure of O₂ near the material to help prevent immediate reoxidation of the oxygen-deficient iron oxide [16]. This two-step reaction also provides an advantageous solution to H₂ and O₂ separation since the products are generated in separate reaction steps.

The advantages of using iron oxides include that they are abundantly available and non-corrosive. Iron oxides are, also, non-volatile and remain in solid state during the reaction cycle facilitating the separation of products from the reactive material, which is particularly important in the regeneration of the active oxygen-deficient material [3,17-20]. For most synthesis procedures, Fe₂O₃ is the initial iron oxide state formed. Activation of the material is done by

thermal reduction, which reduces Fe_2O_3 to Fe_3O_4 and then to the active FeO [3,21]. Ideally all of the Fe_3O_4 present in the material after WS is reduced to FeO , but due to sintering (and thus diffusion limitations [22]) it is more likely that the iron oxide present in the material during the thermochemical cycles is a mixture of Fe_3O_4 and FeO .

The main limitation of thermochemical cycles is the high processing temperature for the thermal reduction (TR) step (1,500 °C). At these high temperatures, the unsupported iron oxide materials suffer from rapid deactivation due to severe sintering (particle growth and agglomeration) and melting during the reduction of Fe_3O_4 to FeO (melting points of Fe_3O_4 and FeO are 1,538 °C and 1,377 °C, respectively) [23,24]. An approach to enhancing the iron oxide reaction and avoiding severe sintering is to deposit the iron oxide on a high-temperature, thermal shock resistant support, such as zirconia [10,20,25-29]. Zirconia helps to reduce sintering and coagulation of iron oxide during high temperature processes, specifically in the temperature range of 1,000 - 1,400 °C due to its higher melting temperature (2,715 °C) compared with iron oxides [27,30]. The zirconia support itself can also be stabilized with various dopants, such as yttria-stabilized zirconia (YSZ), and used as supports for the iron oxide. Literature data indicate that iron can be incorporated in the YSZ lattice during thermal treatment, which can reduce sintering by impeding grain growth [31] and improve reproducibility between cycles [27,32].

In this investigation, the interactions between the reactive iron oxide and the nanoparticle zirconia support were examined in detail as a function of iron loading and yttria-dopant addition. Although previous studies [10,20,25-29, 32-34] have investigated the reactivity of zirconia-supported and yttria-stabilized zirconia-supported iron oxides, no study has characterized these materials in detail and critically compared different zirconia supports to further the understanding of these materials in the production of hydrogen via thermochemical water

splitting. In this study, nanoparticle zirconia supports were used in an attempt to increase the interaction between the iron oxide and the zirconia support, and the results were compared to iron oxide supported on a conventional zirconia support. Zirconia nanoparticles have been used favorably in previous water-splitting studies, but only with chemical reduction and not with the high temperatures needed for thermal reduction [29]. The materials in this study were characterized in detail using X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) to determine how the materials properties affect the activity and cyclic behavior.

2. Experimental

2.1 Material Synthesis

The reactive materials were prepared using commercially available nanoparticle powders of zirconia (n-ZrO₂) and 8 mol% yttria-stabilized zirconia (n-YSZ) supplied by Nanostructured & Amorphous Materials Inc, as well as a porous zirconia pellet (p-ZrO₂) support supplied by Alfa Aesar. The FeO_x materials supported on the n-ZrO₂, n-YSZ and p-ZrO₂ were prepared by a previously reported precipitation method [35]. One material was also prepared using the incipient wetness impregnation (IWI) method to deposit iron oxide onto the porous ZrO₂ support pellets.

In the precipitation method, an aqueous solution of metal nitrate (Fe(NO₃)₃·9H₂O (Alfa Aesar, 98.0-101.0%) was added to an aqueous dispersion of the support (either n-ZrO₂ or n-YSZ). The resulting mixture was titrated with a sodium hydroxide solution (NaOH, Sigma-Aldrich, 99.99% trace metals basis) until the pH of the mixture was in the range of 9-10 to form iron hydroxides on the support. The amount of NaOH added corresponded to a 100% excess

based on the amount of metal nitrate used. The resulting mixture was aged overnight at room temperature before being filtered. The filtered material was rinsed in deionized (DI) water, aged overnight at room temperature, and filtered again. The material was then dried in air at 105 °C overnight and calcined in air at 800 °C for 4 h. This was a low calcination temperature for these materials, as the reaction temperature was as high as 1,500 °C. However, it was discovered that calcination in static air above 1,000 °C in some cases melted the material into a dense hard mass. Therefore, further heat treatment (to 1,500 °C) was done under an inert flow of helium and argon in the reactor system. This heat treatment was part of the activation step (see below), and the materials were held at 1,500 °C longer than in subsequent thermal reduction steps to obtain a stable material during the succeeding reaction cycles. Each material prepared had different iron loadings, and the amount of iron metal in the final material was varied between 5 and 20 weight percent (wt%). The final material was then pressed into a pellet, crushed, and sieved to obtain a powder with particle sizes in the range of 500-710 μm . One reference material was also prepared by crushing the porous ZrO_2 pellets (to obtain the same particle size as for the nanoparticle ZrO_2 supports) and depositing the iron oxide (10 wt% iron loading) using the precipitation method described above.

For the reference material prepared using the IWI method, the iron nitrate precursor was dissolved in a volume of DI water equal to the pore volume of the pellet support. The 0.32 cm (1/8") ZrO_2 pellet support was dried at 105 °C over night before drop-wise addition of the dissolved precursor until incipient wetness during continuous stirring. This material then underwent the same drying and calcination procedures as described above for the precipitation method and was used in this form for reaction experiments.

2.2 Reactor set-up

A reactor was designed and built to allow both the water splitting (WS) and thermal reduction (TR) steps to occur sequentially. Many previous studies have utilized two separate reactor systems, one for WS and one for TR [3,19,24,27,28,36]. Two reactor systems can be used when the material must be pulverized outside of the system, to alleviate the significant particle agglomeration (sintering) that occurs during the TR step, before being transferred to the WS reactor system. Our goals were to eliminate the pulverization step and design a material that can be tested in one reactor without the need for material handling or exposure to air between cycles.

A schematic of the reactor system is shown in Figure 1. The reactive material, in this case zirconia-supported iron oxide (Fe_2O_3), was loaded into a 0.95 cm (3/8") inner diameter (ID) [1.27 cm (1/2") outer diameter (OD)] alumina tube, which was then placed inside of a separate 5.08 cm (2") OD alumina tube, housed in a Carbolite STF 16/450 1600 °C tube furnace equipped with a programmable temperature controller. The reactor effluent passed through a condenser (an ice bath) to cool the gases and remove most of the unreacted water, before being analyzed by an on-line mass spectrometer (Hidden QGA Gas Analyzer) to determine the product gas composition.

Each reaction cycle consisted of two steps where the material was first activated by heating at a constant rate of 10 °C/min to 1,500 °C (operating temperature for thermal reduction), under a flow of inert; a mixture of argon and helium (1:1) at a total flow rate of 40 standard cm^3/min . Helium was used as the internal standard in the mass spectrometer, and argon was used to increase the thermal conductivity of the gas stream to avoid heat transfer issues. The argon and helium streams were fed to the system via two separate AliCat mass flow controllers. The reactive material was held at 1,500 °C until there was no more oxygen released, resulting in

an oxygen-deficient material (FeO supported on ZrO₂ or YSZ). At this time, the reactor temperature was decreased to 1,000 °C and the reactor was switched to WS mode.

For the WS step, a KDS series 101 syringe pump injected 0.3 mL per minute of deionized water into an evaporator (a MTI GSL-1100X tube furnace), held at 120 °C, to generate steam. The steam was carried by the inert gases, argon and helium (1:1 ratio at 40 cm³/min), through heated lines to the reactor furnace. When steam passed over the oxygen-deficient iron oxide at 1,000 °C, the water decomposed, hydrogen was released, and oxygen was taken up by the oxygen-deficient iron oxide resulting in oxidation to Fe₃O₄. When no more hydrogen was detected, the syringe pump was turned off, so that no more water entered the evaporator, and the reactor was flushed with the inert gases for 20 minutes before the temperature was increased to 1,500 °C and the reactor entered TR mode again regenerating the active, oxygen-deficient iron oxide material (supported FeO). For each WS experiment, the contribution of water to the H₂ signal was evaluated and, although very small, subtracted from the MS data for consistency and accuracy.

Figure 1. Flow diagram of the water-splitting reactor system. MFC: mass flow controller, TC: thermocouple, and MS: mass spectrometer.

The WS and TR cycles were repeated six or ten times to determine the hydrogen production and oxygen evolution in each step and how these vary as a function of time (or cycle), to reveal the stability of the materials.

2.3 Material Characterization

The specific surface areas (SSAs) of the support materials and the prepared reactive materials, before and after reaction, were determined by a 6-point Brunauer-Emmett-Teller (BET) method on a Quantachrome NOVA 1200 instrument.

The morphology of the reactive iron materials was analyzed before and after WS cycles using a FEI XL-40 field emission scanning electron microscope (FEG-SEM). Samples were

mounted and prepared with a carbon coating. Elemental mapping of the sample materials was performed using energy-dispersive X-ray spectroscopy (EDS) to locate the iron and its distribution on the material's surface.

Room temperature X-ray diffraction (XRD) patterns were gathered on a Phillips X'Pert Powder X-ray diffractometer using Bragg-Brentano geometry and Cu K α radiation ($\lambda = 0.154$ nm). Selected material powders were secured onto a glass slide with double-sided tape prior to measurements. An average crystallite size was calculated using the Scherrer equation (Equation 1).

$$d_p = \frac{K\lambda}{\beta \cos \theta} \quad \text{Eq. 1}$$

In the Scherrer equation, d_p is the crystallite size (nm), K is the shape factor (taken as 0.9), λ is the radiation wavelength (nm), β is the peak width at half the maximum intensity, and θ is the Bragg angle (radians).

Lattice parameter calculations were included to determine if any expansion or contraction of the unit cell occurred as a result of iron being incorporated into the support lattice crystal structure. The monoclinic (n-ZrO₂ and p-ZrO₂) and cubic (n-YSZ) lattice structures have the following relationship between the planar values (h , k , and l), lattice axial angle (β), lattice axial distances (a , b , and c), and the d-spacing (d) (Eq. 2 and 3) along with the Bragg equation (Eq. 4).

$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right) \quad \text{Monoclinic, Eq. 2}$$

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad \text{Cubic, Eq. 3}$$

$$n\lambda = 2d \sin \theta \quad \text{Eq. 4}$$

Reference values of $a = 5.151 \text{ \AA}$, $b = 5.203 \text{ \AA}$, $c = 5.316 \text{ \AA}$, $\beta = 99.196^\circ$ (JCPDS #: 98-006-0900) for monoclinic ZrO_2 and $a = 5.145 \text{ \AA}$ (JCPDS #: 98-017-3694) for cubic n-YSZ were used for comparison.

3. Results and Discussion

The prepared materials, iron oxide on various zirconia supports ($\text{FeO}_x/\text{n-ZrO}_2$, $\text{FeO}_x/\text{n-YSZ}$, or $\text{FeO}_x/\text{p-ZrO}_2$), at different iron loadings between 5 and 20 wt%, were subjected to cyclic thermochemical water splitting (WS) experiments and detailed material characterizations.

3.1 WS H_2 Production

For each experiment, the prepared powder material was loaded into the packed bed reactor system described above and thermally activated by heating the reactor furnace up to $1,500^\circ\text{C}$ to generate the oxygen-deficient iron oxide for the WS step. Cycles of WS and TR were repeated for the iron oxide supported on the different ZrO_2 ceramics (n- ZrO_2 , n-YSZ, or p- ZrO_2) and the hydrogen production during the WS step was evaluated as a function of cycle number and iron metal loadings (between 5 and 20 wt%). The results are presented in Table 1 and Figures 2 and 3.

Figure 2. Hydrogen production as a function of thermochemical cycle for (a) ZrO_2 supported materials (n- ZrO_2 : nanoparticle zirconia, and p- ZrO_2 : pellet zirconia prepared via precipitation {PPT} or incipient wetness impregnation {IWI}) and (b) yttria stabilized nanoparticle zirconia (n-YSZ) supported materials. Error bars for each material are given in Figure 3.

From Figure 2 it is evident that most of these materials are rather stable after the first cycle. Further particle growth would be expected during subsequent TR steps, particularly considering the fact that nanoparticles were used as the supports. However, the data in Figure 2 reveal that particle growth in subsequent steps is limited and is only notable for the materials with the highest iron loadings. The hydrogen production values over these materials are similar [27,32] or even better [34] than previously reported values.

A few trends are observable in Figure 2. The $\text{FeO}_x/\text{n-YSZ}$ results in a higher hydrogen production for all iron loadings compared with $\text{FeO}_x/\text{n-ZrO}_2$ and $\text{FeO}_x/\text{p-ZrO}_2$, and the hydrogen production varies more with iron loading on the $\text{FeO}_x/\text{n-ZrO}_2$ compared with the $\text{FeO}_x/\text{n-YSZ}$ supported material. Therefore, there is a more distinct optimal iron loading on the $\text{FeO}_x/\text{n-ZrO}_2$ (10 wt% Fe), but also the $\text{FeO}_x/\text{n-YSZ}$ materials exhibit a better performance at 10 wt% iron loading. At an iron metal loading of 5 wt%, the reaction is limited by the amount of iron that is available for reaction, while at the highest iron metal loading (20 wt%), the iron is not stabilized by the support and severe sintering of the iron likely occurs which reduces the amount of iron oxide that is available to react. The latter is evident as a decrease in hydrogen production with increasing reaction cycles (Figure 2b). Since the iron loading varies between materials and thus the amount of iron in the reactor is different, a hydrogen production per unit weight of iron (in addition to the hydrogen production per unit weight of material) is also reported in Table 1 and Figure 3 to obtain a measure of the iron utilization in these materials.

Table 1. Hydrogen production over zirconia-supported FeO_x materials

	H ₂ Production Values					
Material (Iron weight loading) ^a	Average [cm ³ /g material]	Average [cm ³ /g Fe]	Initial (WS Cycle 1) [cm ³ /g material]	Final (WS Cycle 10) [cm ³ /g material]	SSA Fresh [m ² /g]	SSA Spent [m ² /g]
FeO _x /n-ZrO ₂ :						
5 wt% Fe	0.8	16	1.2	0.9 ^b	8.5	0.8
10 wt% Fe	2.0	20	2.4	1.8	9.7	1.2
15 wt% Fe	1.2	8.3	1.8	1.1	10.2	1.1
20 wt% Fe	1.4	7.1	2.2	1.2	8.4	0.7
FeO _x /p-ZrO ₂ :						
10 wt% Fe-PPT	1.2	12	1.6	1.0 ^b	23.3	0.9
10 wt% Fe-IWI	0.4	4.0	0.6	0.4 ^b	23.0	0.9
FeO _x /n-YSZ:						
5 wt% Fe	2.8	57	2.7	3.1 ^b	12.9	1.0
10 wt% Fe	3.4	34	3.9	2.9	10.2	1.7
15 wt% Fe	2.9	19	3.1	2.9 ^b	6.7	0.7
20 wt% Fe	2.5	12	3.5	2.0	8.1	1.5

^a PPT: material prepared via precipitation on a crushed p-ZrO₂ support and IWI: material prepared via incipient wetness impregnation in the ZrO₂ pellets.

^b This denotes the final H₂ production for a material that was only run through six water splitting cycles instead of ten.

Figure 3. Average hydrogen production (per unit weight of iron versus per unit weight of material) for six or ten cycles for $\text{FeO}_x/\text{n-ZrO}_2$, $\text{FeO}_x/\text{p-ZrO}_2$, and $\text{FeO}_x/\text{n-YSZ}$ materials. ■ : 5 wt% $\text{FeO}_x/\text{n-YSZ}$, ● : 10 wt% $\text{FeO}_x/\text{n-YSZ}$, ▲ : 15 wt% $\text{FeO}_x/\text{n-YSZ}$, ◆ : 20 wt% $\text{FeO}_x/\text{n-YSZ}$, □ : 5 wt% $\text{FeO}_x/\text{n-ZrO}_2$, ○ : 10 wt% $\text{FeO}_x/\text{n-ZrO}_2$, △ : 15 wt% $\text{FeO}_x/\text{n-ZrO}_2$, ◇ : 20 wt% $\text{FeO}_x/\text{n-ZrO}_2$, ★ : 10 wt% $\text{FeO}_x/\text{p-ZrO}_2$ - PPT, ☆ : 10 wt% $\text{FeO}_x/\text{p-ZrO}_2$ - IWI

As expected, the lower iron loadings are utilizing more of the iron present in the material, and this is clearly evident in Figure 3. For $\text{FeO}_x/\text{n-ZrO}_2$ materials, a 10 wt% iron loading clearly is the optimal material, as it gives the highest hydrogen yield per unit weight of material and per unit weight of iron. The lower hydrogen yield per unit weight of iron for the 5 wt% $\text{FeO}_x/\text{n-ZrO}_2$ material may indicate that some of the iron is interacting too strongly with the n- ZrO_2 support and is not available for reaction on this material. Since the variation in hydrogen yield as a

function of iron loading is smaller over the $\text{FeO}_x/\text{n-YSZ}$ materials, determining the optimal material composition is not as straight forward. Since the average H_2 production is in the range between 2.5 and 3.4 cm^3 per gram of material for the various iron loadings, the yield per unit weight of iron is very different. The highest hydrogen production per unit weight of material is obtained over the 10 wt% $\text{FeO}_x/\text{n-YSZ}$ material, but since the hydrogen yield is only slightly lower, the yield per unit weight of iron is considerably higher for the 5 wt% $\text{FeO}_x/\text{n-YSZ}$ material (Table 1, Figure 3). Increasing the iron loading to 15 wt% does not improve the average hydrogen yield per unit weight of material, and the hydrogen yield per unit weight of iron is therefore significantly lower than for the 10 wt% $\text{FeO}_x/\text{n-YSZ}$. If the iron loading is increased to 20 wt% the support can no longer stabilize the iron oxide on the surface, and the hydrogen yield decreases with increasing reaction cycle.

The reactive materials synthesized through the precipitation method onto the nanoparticle supports perform remarkably better than the 10 wt% $\text{FeO}_x/\text{p-ZrO}_2$ prepared through the incipient wetness impregnation method on the ZrO_2 pellets. This material has a significantly lower hydrogen production and yield in comparison and performs below all other tested materials. The interaction between the pellet support and the iron oxide may not be sufficient to stabilize the material and overcome the detrimental agglomeration and melting effects evident in pure iron oxide water splitting reactions. The 10 wt% $\text{FeO}_x/\text{p-ZrO}_2$ prepared using the precipitation method on the crushed ZrO_2 pellets performs better than the $\text{FeO}_x/\text{p-ZrO}_2\text{-IWI}$, but does not quite reach the performance of the 10 wt% $\text{FeO}_x/\text{n-ZrO}_2$ prepared using the same precipitation method. Consequently, there is a significant benefit to using nanoparticle oxide supports in the preparation of these materials.

Comparing the iron supported on the two zirconia-based nanoparticle supports, the FeO_x/n-YSZ materials have a higher average H₂ production per unit weight of material compared with all the iron loadings of the FeO_x/n-ZrO₂ materials. Thus for the same iron loading, the hydrogen yield per gram of iron is higher for the n-YSZ supported material than for iron supported on n-ZrO₂. While the hydrogen yield per unit weight of reactive metal (oxide) is important in the characterization of these materials, ultimately, the more important number is the hydrogen production per unit weight of material, since n-ZrO₂ is more expensive than FeO_x [37,38] and the amount of material added into the solar reactor should be minimized.

3.2 Material Characterizations

Each material was subjected to BET, SEM, and XRD analysis before (fresh) and after (spent) six or ten WS cycles to characterize the materials and determine properties that affect activity in each cycle, reproducibility between cycles, and to examine interactions between the iron oxide and the ZrO₂ support.

3.2.1. BET Surface Area Measurements

The specific surface area is an important property of a reactive material, since it reveals the surface area available for reaction. At the high temperatures of the water-splitting reaction, loss of surface area due to sintering (particle growth) can be severe, and the reaction quickly becomes diffusion limited, as reacting species must travel through an increasingly thicker layer to reach any active iron species.

The BET surface areas for fresh and spent materials are presented in Table 1. The unsupported n-ZrO₂ and n-YSZ have specific surface areas (SSA) of 8.3 and 13 m²/g

respectively, while SSA of the p-ZrO₂ is 79 m²/g. As expected from the higher support surface area, the material with the largest initial surface area is the 10 wt% FeO_x/p-ZrO₂ (23 m²/g). For the FeO_x/n-ZrO₂ materials, the SSAs are actually higher than the support SSA and increase (from 8.5 to 10.2 m²/g) with Fe loading up to 15 wt%. In contrast, the specific surface areas for the FeO_x/n-YSZ decrease with increasing Fe loading (from 12.9 to 8.9 m²/g). This indicates that the added iron is increasing the overall surface area of the lower surface area support (n-ZrO₂), while for the n-YSZ the iron is blocking some of the pores (or voids) in the support which results in a decrease in surface area with increasing Fe loading for this material.

The SSA measurements of the spent materials are an order of magnitude lower than the fresh materials and range from 0.7 to 1.7 m²/g. The largest decrease in surface area (from 23 to 0.9 m²/g) is observed for the FeO_x/p-ZrO₂-IWI material, which had the largest initial surface area. This severe decrease in surface area contributes to the poor performance of this material. However, this is not the only reason this material is inferior, since the surface area of the spent FeO_x/p-ZrO₂ material is similar to the SSA of the FeO_x supported on either n-ZrO₂ or n-YSZ. A drastic decrease in surface area at the high operating temperatures of this reaction would be expected when using a nanoparticle oxide support. However, it appears that the nanoparticle oxide supports are more efficient in stabilizing the iron oxide on the support compared with the p-ZrO₂ support.

As the heat treatments of the fresh materials were done at 800 °C a series of BET measurements were collected for select materials after the initial activation as well as after subsequent WS and TR steps (not shown) to evaluate the extent of decrease in SSA as a function of thermochemical cycle. After the first activation step, the SSAs for the 10 and 20 wt% materials on the n-ZrO₂ and n-YSZ supports were all in the range of 1.3 to 1.8 m²/g. The

measurements for the next three steps remained within $\pm 0.4 \text{ m}^2/\text{g}$ of these values, which is within the range of the SSAs measured on the spent materials after six to ten cycles. This indicates that the majority of the iron oxide particle growth occurred during the first activation procedure and once the reactive materials have been activated, they are rather stable and minimal particle growth occurs with subsequent water-splitting cycles. Comparing the FeO_x supported on n- ZrO_2 and n-YSZ it appears that the spent $\text{FeO}_x/\text{n-YSZ}$ materials have slightly higher SSAs, despite the lower fresh SSA. This is consistent with cubic zirconia (the crystalline phase of YSZ) being the more stable phase at high temperatures compared with monoclinic ZrO_2 . However, the differences in SSAs are not sufficiently large to explain the observed differences in hydrogen yield, and there is no simple correlation between the surface area of the spent materials and the hydrogen yield.

3.2.2. SEM Analysis

Select fresh and spent materials, 10 wt% $\text{FeO}_x/\text{n-ZrO}_2$ and 10 wt% $\text{FeO}_x/\text{n-YSZ}$, were analyzed using SEM, and representative images are presented in Figures 4a, b, e and f. Energy dispersive X-ray spectroscopy (EDS) line scans and mapping confirms the presence of iron, oxygen, zirconium (and yttrium for the n-YSZ support) on the surface for the fresh and spent materials. The results of the EDS mapping are presented for Fe in Figures 4c, d, g and h. The two fresh materials have similar particle sizes (Figures 4a and b), and EDS mapping reveals that they have a homogenous distribution of each component with no distinct segregation of iron or zirconium oxides for either supported materials (Figures 4c and d). Significant particle growth due to sintering is evident when comparing the SEM images obtained from the fresh and spent materials (Figure 4). After several reaction cycles, the $\text{FeO}_x/\text{n-YSZ}$ material appears to exhibit a

more significant particle growth/sintering effect of the support and the grain boundaries appear more fused together compared to the $\text{FeO}_x/\text{n-ZrO}_2$ material (Figures 4e and f). EDS mapping also reveals that both reactive materials exhibit iron oxide particle growth on the surfaces of the zirconia supports after the reaction cycles (Figure 4g and 4h), and significant iron segregation has occurred. The large iron-rich regions in the EDS map of the $\text{FeO}_x/\text{n-ZrO}_2$ material (Figure 4g) are visible also in the SEM image (Figure 4e), due to the difference in morphology between the iron and zirconium oxides. In contrast, the iron-rich particles of the $\text{FeO}_x/\text{n-YSZ}$ cannot be observed in the SEM image (Figure 4f). The EDS map is needed (Figure 4h) to identify presence of iron oxide particles. The difference between the $\text{FeO}_x/\text{n-ZrO}_2$ and $\text{FeO}_x/\text{n-YSZ}$ materials could be that the yttria-stabilized zirconia has a morphology that is similar to the iron oxide, or the YSZ has encapsulated the iron oxide.

Figure 4. SEM images of fresh (a) and spent (e) 10 wt% $\text{FeO}_x/\text{n-ZrO}_2$ and fresh (b) and spent (f) 10 wt% $\text{FeO}_x/\text{n-YSZ}$. Energy dispersive spectroscopy (EDS) was used to map out elemental components in the SEM images, the EDS map for Fe K α signals is shown in (c), (d), (g) and (h) for 10 wt% $\text{FeO}_x/\text{n-ZrO}_2$ and 10wt% $\text{FeO}_x/\text{n-YSZ}$ fresh and spent, respectively.

3.2.3. XRD Measurements

XRD patterns for the fresh and spent reactive materials are shown in Figure 5. The figure clearly reveals that the ZrO_2 is present in different phases for the two nanoparticle zirconia supports, i.e. the n- ZrO_2 support is monoclinic and the n-YSZ support is cubic. The main iron oxide phase of the fresh materials is Fe_2O_3 while the spent materials have Fe_3O_4 present in the bulk of the material. The calculated particle sizes from the Scherrer equation are presented in Table 2 and reveal a few trends which are also evident in the XRD patterns from the peak intensities and peak widths. Comparing all materials, the particle sizes of the zirconia supports increased slightly between fresh and spent, while the average iron oxides particle size decreased. There is not a continuous trend in iron oxide particle size with iron loading, but the Fe_3O_4 particle sizes for spent materials with high iron loading appear to be smaller than the Fe_2O_3 particle size on the original fresh material. This is likely due to incomplete reduction of the original Fe_2O_3 .

Considering the high reaction temperatures, the crystallite sizes remain surprisingly small for nanoparticle supports. Spent materials also exhibit a lower signal-to-noise ratio which may be due to a reduction in the number of sampled grains due to particle size, texturing effects, reduced crystallinity or crystalline quality, poor packing of the material, or a combination of these. The $\text{FeO}_x/\text{p-ZrO}_2$ material exhibits a very different behavior compared with the $\text{FeO}_x/\text{n-ZrO}_2$ material, even though both supports consist of monoclinic zirconia. While the crystallite size of n- ZrO_2 increases from 21 to 32 nm during the reaction cycles, the average crystallite size of the p- ZrO_2 support increases from 17 to 40 nm (Table 2). The $\text{FeO}_x/\text{p-ZrO}_2$ material appears more crystalline after reaction, likely due to a larger number of sampled grains, while the

opposite is true for the $\text{FeO}_x/\text{n-ZrO}_2$ material. Furthermore, the peaks due to iron oxides are difficult to discern in the XRD pattern obtained from the $\text{FeO}_x/\text{p-ZrO}_2$ materials.

The intensities of Fe_2O_3 peak ($2\theta = 33.2^\circ$) and Fe_3O_4 peak ($2\theta = 35.7^\circ$) increase as the iron loading increases on both nanoparticle-supported materials (Figure 5). Comparing $\text{FeO}_x/\text{n-ZrO}_2$ and $\text{FeO}_x/\text{n-YSZ}$ materials with the same iron loading, the iron oxide features for the n-YSZ supported materials are less prominent than for the n- ZrO_2 materials. The smaller iron oxide features for $\text{FeO}_x/\text{n-YSZ}$ may be due to some iron incorporation into the cubic YSZ lattice, as suggested by Coker et al. [26].

Figure 5. XRD patterns obtained from $\text{FeO}_x/\text{n-ZrO}_2$ and $\text{FeO}_x/\text{n-YSZ}$ fresh (a) and spent (b) materials. ∇ : monoclinic ZrO_2 , $\blacktriangledown$: cubic YSZ, $\bullet$ (red): Fe_2O_3 (JCPDS #: 98-002-2505) and $\bullet$ (blue): Fe_3O_4 (JCPDS #: 98-015-8745).

Figure 6. XRD patterns obtained from fresh and spent $\text{FeO}_x/\text{n-ZrO}_2$ and $\text{FeO}_x/\text{p-ZrO}_2$ -IWI materials with 10 wt% Fe loading. ∇ : monoclinic ZrO_2 , $\bullet$ (red): Fe_2O_3 , and $\bullet$ (blue): Fe_3O_4 .

Table 2. Average crystallite sizes (in nm) calculated using the Scherrer equation for the supports and select FeO_x/n-ZrO₂, FeO_x/p-ZrO₂, and FeO_x/n-YSZ materials before (fresh) and after (spent) six or ten reaction cycles.

Material ^a	Support ^{b,c}		5 wt% loading		10 wt% loading		15 wt% loading		20 wt% loading	
	Fresh	Spent	Fresh	Spent	Fresh	Spent	Fresh	Spent	Fresh	Spent
FeO _x /n-ZrO ₂ materials:										
n-ZrO ₂	15.6	38.1	25.9	30.9 ^c	21.2	32.3	29.6	32.5	29.3	36.1
Fe ₂ O ₃	---	---	39.8	---	21.7	---	31.8	---	34.2	---
Fe ₃ O ₄	---	---	---	26.3 ^c	---	21.9	---	21.3	---	29.6
FeO _x /n-YSZ materials:										
n-YSZ	29.1	41.3	28.9	45.5 ^c	28.0	43.2	31.2	39.0 ^c	31.8	30.6
Fe ₂ O ₃	---	---	36.0	---	29.5	---	43.0	---	41.6	---
Fe ₃ O ₄	---	---	---	35.8 ^c	---	28.7	---	28.2 ^c	---	34.2
FeO _x /p-ZrO ₂ :										
p-ZrO ₂	10.7	---	---	---	17.3	39.8	---	---	---	---

^a Fresh material: data obtained after calcination at 800 °C for 4 hours. Spent material: data obtained after 10 reaction cycles, unless noted otherwise.

^b This material went through the same procedures as the supported iron materials: support powder was heat treated at 800 °C (fresh) and then subjected to WS cycles (spent).

^c Crystallite size after six cycles.

To obtain a better understanding of the iron incorporation and iron solubility within the YSZ and ZrO₂ lattices, the XRD patterns of the fresh and spent materials were investigated by evaluating the shifts in the lattice. Even though the iron oxide features in the FeO_x/n-YSZ materials are less pronounced compared with the FeO_x/n-ZrO₂ materials (and it is therefore challenging to evaluate differences between the materials using these peaks), important information can be obtained from the ZrO₂ and YSZ peaks. A large shift in 2θ values of the ZrO₂ peaks is evident after iron deposition (Figure 7), which suggests iron incorporation into the ZrO₂ lattice. When the iron enters the zirconia lattice structure, the iron cations replace the yttrium or zirconium cations at their lattice points. Since the iron cations are smaller in size, this replacement causes the lattice to contract decreasing the unit cell size of the n-YSZ. A contraction in the lattice due to iron incorporation therefore leads to a decrease in the lattice

parameters, a , b , c , and β . (Eq. 2 and 3) and an increase in the 2θ value (Eq. 4) which is observed experimentally in Figure 7.

Figure 7. XRD patterns obtained from all spent $\text{FeO}_x/\text{n-ZrO}_2$ and $\text{FeO}_x/\text{n-YSZ}$ materials. The black dashed lines indicate the position of the reference monoclinic n- ZrO_2 or cubic n-YSZ peaks while the blue dotted lines indicate the 2θ values of the reference Fe_3O_4 . ∇ : ZrO_2 , $\blacktriangledown$: n-YSZ, $\bullet$: Fe_3O_4 .

The unit cell volumes for the ZrO_2 supports, calculated using Equations 5 and 6, are displayed in Figure 8, for fresh and spent materials as a function of iron loading.

$$V = abc \sin \beta \quad (\text{Monoclinic}) \quad \text{Eq. 5}$$

$$V = a^3 \quad (\text{Cubic}) \quad \text{Eq. 6}$$

Iron incorporation into the ZrO_2 unit cell does occur for all fresh materials as the unit cell volume of ZrO_2 is smaller for all iron loadings compared to the reference unit cell volume sizes

of 140.64 and 136.19 Å³ for ZrO₂ and n-YSZ respectively. This is consistent with what is generally seen for doped materials in the applications of Vegard's law, where a smaller dopant enters the lattice of a host with larger cations [39]. The iron incorporation seen through the lattice contraction is more extensive than what has been previously reported for fresh materials prepared by conventional solid state synthesis at 1,450 or 1,500 °C [26]. The more extensive lattice incorporation may be due to the precipitation method employed here and the nanoparticle ZrO₂ support. The nanoparticle support likely has more surface defects and this together with the precipitation method could lead to strong FeO_x-ZrO₂ interactions. The high temperature heat treatments could also increase lattice flexibility which in turn leads to more of the iron entering into the unit cell of zirconia. The presence of other components, such as yttrium ions, may also play an important role in determining the amount of iron incorporation, as the cubic zirconia phase may accommodate iron easier than the monoclinic zirconia.

For both supports (n-ZrO₂ and n-YSZ), the fresh materials exhibit a decrease in unit cell volume with an increase in the amount of iron that was precipitated onto the support. This decrease with increasing iron loading indicates a higher degree of iron incorporation with increased loading, at least up to a 15 wt% iron loading. It appears that a 15 wt% iron loading results in a lower extent of iron incorporation than either a 10 wt% or 20 wt% iron loadings for both FeO_x/n-ZrO₂ and FeO_x/n-YSZ materials. It is possible that 15 wt% iron is near the solubility limit, so that segregation occurs for the fresh materials and iron particles of a critical size are formed, i.e. iron is pulled out of the lattice again to form particles of a minimum stable size. As more iron is added, it can enter the ZrO₂ lattice again until saturation.

The spent materials exhibit a different trend from the fresh materials. For the spent FeO_x/n-ZrO₂ materials, only the 5 wt% iron loading reveals a smaller unit cell volume than the

cycled n-ZrO₂ reference. All the other spent FeO_x/n-ZrO₂ materials have similar unit cell volumes to that of the reference material with no iron content. This suggests that there is some phase separation during water splitting forming segregated iron oxide and zirconia particles, which is consistent with observations in the SEM images (Figure 4e).

The behavior of the spent FeO_x/n-YSZ materials differs from the FeO_x/n-ZrO₂ in that the unit cell volume decreases with increasing iron loading between 0 and 15 wt%. This indicates that a significant amount of the iron that originally entered into the support lattice remains incorporated in the unit cell structure, which was not observed for the FeO_x/n-ZrO₂ material. Consistent with the results for the fresh materials, it appears that 15 wt% iron is the maximum amount of iron that can enter the lattice and any additional iron will segregate and form iron oxide particles. For the FeO_x/n-ZrO₂ materials, this unwanted iron oxide segregation happens for most iron loadings which may explain the overall lower H₂ production values seen for these materials versus the FeO_x/n-YSZ materials (Table 1). Excess segregated iron species have a higher tendency to agglomerate and sinter at the high operating temperatures, thus hindering the activity and stability of the materials. SEM images for both spent materials show presence of segregated iron oxide particles, but the spent FeO_x/n-YSZ materials show less distinct iron-rich regions present at the surface compared with the FeO_x/n-ZrO₂ material. These observations, together with the smooth morphology observed on the spent FeO_x/n-YSZ material, are consistent with iron incorporation into the n-YSZ lattice. The fact that iron in the lattice of cubic n-YSZ appears more stable than iron in the monoclinic n-ZrO₂ lattice is consistent with the more stable hydrogen production from the FeO_x/n-YSZ material and may explain the higher hydrogen production over this material.

Figure 8. Unit cell volume (Å³) calculations for fresh and spent FeO_x/n-ZrO₂ (a) and FeO_x/n-YSZ (b) materials for all iron metal loadings studied.

4. Conclusion

High temperature ceramic oxide nanoparticles were used as supports to prepare iron oxide materials for the thermochemical water splitting reaction. The effects of iron loading on

these materials and on the hydrogen yields were carefully examined before and after six or ten thermochemical water splitting cycles, and the materials were compared to iron oxide materials supported on a conventional pellet (porous) zirconia support.

Iron oxide supported on zirconia or yttria-stabilized zirconia nanoparticles exhibited a significantly higher hydrogen production compared with the iron oxide supported on a conventional zirconia support. The materials supported on the zirconia nanoparticle oxides were surprisingly stable after the first water-splitting cycle, where most of the sintering and particle agglomeration took place. Using nanoparticles in the synthesis of the materials appeared to result in more efficient iron-zirconia interactions compared with the conventional support. Rather than depositing iron oxide onto the surface of a stable zirconia support, the use of nanoparticle zirconia may have facilitated iron incorporation into the zirconia support lattice, improving iron-zirconia interactions, thus leading to more stable materials.

The amount of hydrogen produced per WS cycle over these materials increased with the iron loading up to 10 wt % (metal basis). At loadings higher than 15 wt% iron, the stability of the material decreased as evident in the decreased hydrogen yield with each cycle. The lower stability of these materials at higher iron loadings is likely due to weaker iron-zirconia interactions. As the iron content is increased, the zirconia can no longer interact efficiently with all the iron, resulting in more facile iron oxide agglomeration and sintering, leading to particle growth, diffusion limitations, and ultimately a less efficient water-splitting material.

The $\text{FeO}_x/\text{n-YSZ}$ materials consistently resulted in higher hydrogen yields compared with the $\text{FeO}_x/\text{n-ZrO}_2$ materials. It also appears that the $\text{FeO}_x/\text{n-YSZ}$ material was less sensitive to iron oxide loading, as the hydrogen yield varied more with iron loading on this material than over the $\text{FeO}_x/\text{n-ZrO}_2$ materials. While the BET surface areas of the spent $\text{FeO}_x/\text{n-YSZ}$ materials

are slightly higher than those of the spent $\text{FeO}_x/\text{n-ZrO}_2$ and $\text{FeO}_x/\text{p-ZrO}_2$ materials, there is not an evident correlation between the BET surface areas and the hydrogen yield over these materials. The largest drop in specific surface area between fresh and spent materials was observed over the 10 wt% $\text{FeO}_x/\text{p-ZrO}_2\text{-IWI}$, despite the fact that the p-ZrO_2 would be expected to be more stable than n-ZrO_2 . Thus, this indicates that the p-ZrO_2 is less effective in stabilizing the iron oxide on this support compared with the n-ZrO_2 , and this is one reason for the low hydrogen yields from the $\text{FeO}_x/\text{p-ZrO}_2$ materials.

XRD data analysis revealed iron incorporation into the nanoparticle zirconia and yttria-stabilized zirconia support lattices. However, after several reaction cycles, a significant amount of the iron initially incorporated in the n-ZrO_2 support has been expelled from the lattice, resulting in iron segregation. Any iron oxide that segregates out from the support lattice will not be efficiently stabilized by the zirconia, which can result in iron oxide agglomeration and particle growth reducing the activity of the material due to diffusion limitations. Iron oxide segregation was evident in the SEM images of the spent $\text{FeO}_x/\text{n-ZrO}_2$ material. While some segregation did occur on the $\text{FeO}_x/\text{n-YSZ}$, the yttria-stabilized zirconia materials maintained a significant amount of the iron incorporated in the lattice for all iron loadings after reaction cycles. Therefore, the $\text{FeO}_x/\text{n-YSZ}$ materials are more stable than the materials supported on p-ZrO_2 and n-ZrO_2 . This is very important, since stability of the reactive materials is critical at the high-temperatures employed by the thermochemical water splitting reaction. The high stability of $\text{FeO}_x/\text{n-YSZ}$ materials is likely the largest contributing factor to the higher and more consistent H_2 production compared with the $\text{FeO}_x/\text{n-ZrO}_2$ material.

It should be noted that these materials were chosen to study the interactions between zirconia and iron and how they affect the water-splitting properties. For these reasons, it is a

simplified system, and while they show promising H₂ production values they are not optimal since 80-95% of the material is inert in the water splitting cycle and simply adds thermal mass to the system. Future studies will look into modifying the support in order to minimize the amount of inert material in the reactions.

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