SYNTHESIS AND CHARACTERIZATION OF FERRITE MATERIALS FOR THERMOCHEMICAL CO_2 SPLITTING USING CONCENTRATED SOLAR ENERGY

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Introduction

The Sunshine to Petrol effort at Sandia aims to convert carbon dioxide and water to precursors for liquid hydrocarbon fuels using concentrated solar power (CSP). Significant advances have been made in the field of solar thermochemical H_2O- and CO_2-splitting technologies;[1-3] however much of the materials development effort, while empirically-based, has been somewhat trial-and-error. This is due in part to a lack of fundamental research into the behavior of the metal oxides under development under the high temperature conditions present in these cycles. Basic questions such as oxygen transport, surface chemistry, structural changes vs. redox reactions, the effects of synthesis methods and cycling on the material, and the role of supports have not yet been answered.

One such system that shows promise for CSP-driven splitting utilizes yttria-stabilized zirconia (YSZ)-supported ferrite composites. Such materials work via the basic redox reactions:

$Fe_3O_4 \rightarrow 3FeO + 0.5O_2$ (Thermal reduction, TR, >1350˚C)
$3FeO + CO_2 \rightarrow Fe_3O_4 + CO$ (CO_2-splitting oxidation, CDS, <1200˚C)
$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$ (H_2O-splitting oxidation, WS, <1200˚C)

This system was chosen based on a combination of its effectiveness as a H_2O- and CO_2-splitting composite and because an understanding of the basic Fe_2O_3 system hopefully can be used as a basis to understand the more complex systems such as $CoFe_2O_4$ and other substituted ferrites currently under investigation.

It previously has been shown that the ferrite materials are not effective reactive materials on their own; a support of some sort (e.g. ZrO_2, YSZ, HfO_2) is necessary. [1] Effort has been expended in order to begin to elucidate the complex interaction between the ferrite and support (solid solubility, microstructure, reaction kinetics) which is not well-defined at high temperatures and under redox conditions. The design and execution of in-situ experiments to elucidate the chemistry under operating conditions has been a main focus. This includes simulating H_2O- and CO_2-splitting reactions in the lab using temperature-programmed reduction and oxidation, thermogravimetric analysis (TGA), x-ray diffraction (XRD), and scanning electron microscopy (SEM).

Experimental

The iron oxide-YSZ materials were made by SPEX milling Fe_2O_3 powder with 8YSZ powder in the desired proportions. PVA binder was then added, the dried powder was ground with an agate mortar and pestle, and the mixture uniaxially pressed into pellets. The samples were calcined at 1°C /min up to 1100°C to burn out the binder, then sintered at 1375 ºC /2 h, and finally 1500 ºC/2h before cooling to room temperature. The sintered product was re-ground into a powder for xrd analysis.

In situ X-ray diffraction (XRD) experiments utilized a controlled atmosphere, high temperature sample cell. Thermogravimetric analysis (TGA) was performed under TR, WS, and CDS conditions. Bench reactor tests were carried out in a flow reactor consisting of a mullite tube situated in a high-temperature furnace (CSP surrogate). After TR under inert gas, the reactants (H_2O or CO_2) were introduced into the reactor in an inert sweep stream, and the reactor effluent was monitored by gas chromatography.

Results and Discussion

Samples of Fe_2O_3:YSZ were tested on a bench-top apparatus to measure the amounts of H_2 and CO produced from the H_2O- and CO_2-splitting reaction, respectively. Figure 1 shows the results of multiple cycles for a sample of 5 weight% Fe_2O_3 on 3YSZ (3 mole-%Y_2O_3 in ZrO_2). Several observations can be made:

- CO_2 and H_2O splitting was demonstrated over multiple temperature cycles ;
- % Fe utilization differed between single-source (CO_2 *or* H_2O) and mixed (CO_2 *plus* H_2O) feeds; and
- Material performance had not reached steady-state after multiple cycles. This was also observed in redox experiments on a TGA.

In order to elucidate the reasons behind these observations,

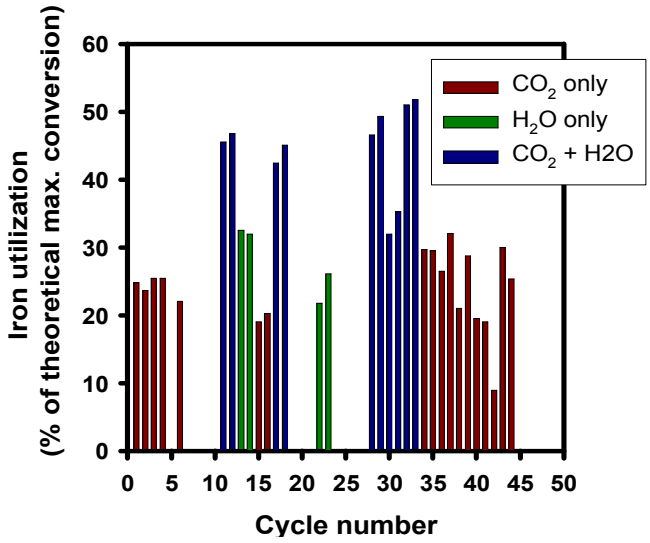

Figure 1: CO_2 and H_2O splitting cycles of 5 wt% Fe_2O_3 on 3YSZ. Iron utilization % max theoretical assumes full conversion between $Fe_3O_4 \rightarrow FeO$.

we have begun to structurally characterize these materials in-depth using XRD and SEM. SEM images of as-synthesized monoliths of Fe_2O_3:8YSZ revealed several interesting microstructural features. When doped with 3 wt% Fe_2O_3, the sample was homogeneous, implying a complete solid solution had formed (i.e., all of the Fe had dissolved into the support). EDS analysis confirmed this observation. However in samples containing 10 wt% Fe_2O_3, un-reacted Fe_2O_3 remained heterogeneously distributed throughout the sample. There was also evidence that during sample preparation, the Fe_2O_3 became at least partially reduced, melted, and re-precipitated at the surface upon cooling (Figure 2). These findings have resulted in a rethinking of the materials fabrication process, which is currently being refined. In addition, substituted ferrites, such as $Co_xFe_{3-x}O_4$ are being considered due to their higher melting points.

Another important question the current study has addressed is what exactly is the solid solubility of Fe_2O_3 in YSZ? There is not a straightforward answer, as the solubility seems to be influenced by a variety of factors, including temperature, atmosphere, and Y-content of the YSZ. The answer is important because preliminary evidence suggests that the redox properties of the composite are affected by the concentration of ferrite in solid solution. For example, a composite containing 5 wt% Fe_2O_3 has a higher percentage of theoretical ferrite

utilization than one containing 20 wt%. Currently, based on XRD of these composites, the solid solubility at room temperature of Fe_2O_3 is greater than 3 wt% and less than 10 wt%. (Figure 3)

An ongoing series of in-situ X-ray diffraction (XRD) experiments has been designed to investigate the solid solubility

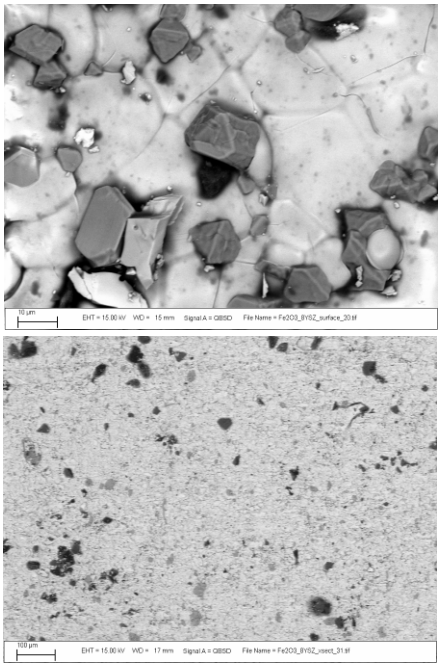

Figure 2: Electron backscattered SEM image of 10 wt% Fe_2O_3:8YSZ (Top) surface showing crystallites (dark) of Fe_2O_3 [illegible]ction

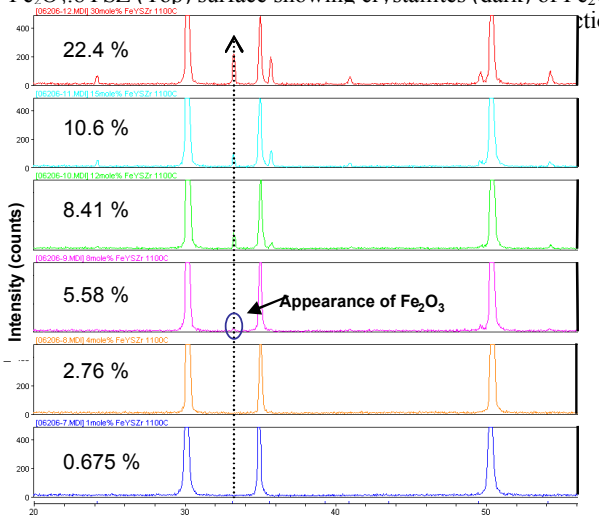

Figure 3: Room temperature XRD of Fe_2O_3 (wt %) in 10% yttria-stabilized zirconia (10YSZ)

question. They involve observing samples with varying Fe_2O_3 concentrations in YSZ as they are heated and cooled under air, CO_2, and He in order to mimic the synthesis and reaction conditions experienced by the reactive material. In one experiment, a composite of 10 wt% Fe_2O_3:8YSZ was heated and cooled under He gas. The initial XRD showed Fe_2O_3 plus a solid solution of Fe in YSZ (cubic ZrO_2 phase). Upon heating, the loss of the Fe_2O_3 peak was observed around 800 °C and a faint signal for Fe_3O_4 formed at ~1150 ºC. Then from ~1250 ºC to 1400 ºC, FeO formed at the expense of Fe_3O_4. At this point the sample was cooled, and the FeO persisted. Figure 4 shows the behavior of the d-spacing for YSZ (111) with temperature during this experiment. These data illustrate that the YSZ lattice parameter does not increase linearly with temperature upon heating. This phenomenon was not observed upon cooling. The decrease in slope was attributed to Fe solubility during heating (i.e., Fe_2O_3 entered YSZ around 800 °C), while the increased slope around 1100 °C correlated with the appearance of Fe_3O_4 as Fe migrated out of the YSZ lattice. Therefore, this seems to be a dynamic behavior, with Fe shuttling between forms, during the heating process. In other words, the solubility of the iron is indeed changing with temperature. Once the FeO has formed, however, it showed stability (in the absence of oxygen), and the YSZ lattice varied linearly with temperature during sample cooling.

Conclusions

We seek to develop a systematic understanding of the Fe_2O_3:YSZ composite materials used in CSP H_2O- and CO_2- splitting

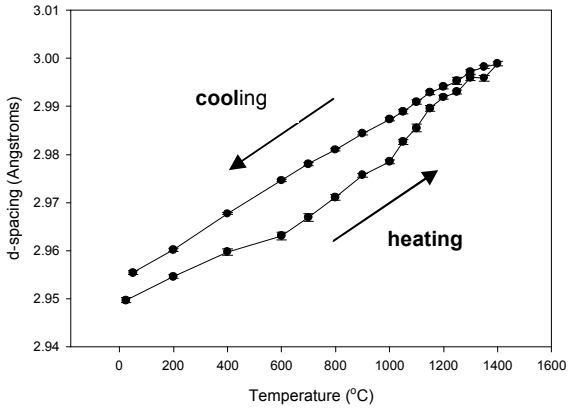

Figure **4:** d-spacing of YSZ (111) peak vs. temperature for 10 wt.-% Fe_2O_3 / 8YSZ sample under He.

reactions, so as to optimize their redox performance and ultimately design new materials with improved efficiency and durability for thermochemical syngas production. Preliminary investigations reveal the ferrites have CO_2-splitting capability, but require a support material for efficient long-term cyclability. However the ferrite-support interaction (solid solubility, microstructure, reaction kinetics) is not well-defined at high temperatures and under redox conditions. Therefore we have designed in-situ experiments to elucidate the chemistry under operating conditions. Preliminary results suggest a mobile iron species in YSZ vs. temperature, which affects the solid solubility of Fe and also the redox activity of the composite. Further analyses utilizing in-situ XRD, microscopy, and TGA are underway.

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