

University of Florida

Development of Novel Water Splitting Catalysts for the Production of Renewable Hydrogen (Progress Report)

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Description: This project focuses on the development of iron-based catalysts for the thermochemical splitting of water into hydrogen and oxygen. The thermochemical process of splitting water is particularly well-suited for the utilization of solar energy to provide the heat for the reaction and is a way to produce a renewable hydrogen fuel. As hydrogen is difficult to transport and store, producing hydrogen on site for power plants using proton exchange membrane (PEM) fuel cells or internal combustion engines to generate electricity or for the production of chemicals, such as liquid hydrocarbon fuels, is a very attractive approach. The project uses a two-step process in which water is passed over a reduced iron oxide to generate hydrogen while the oxygen is taken up by the oxygen-deficient iron oxide (Step 1: $\text{FeO}_{x-1} + \text{H}_2\text{O} \rightarrow \text{FeO}_x + \text{H}_2$). In the second step the resulting iron oxide is heated to desorb oxygen and regenerate the oxygen-deficient iron oxide to close the catalytic cycle (Step 2: $\text{FeO}_x \rightarrow \text{FeO}_{x-1} + \frac{1}{2}\text{O}_2$). The main objectives of the project are to develop mixed metal oxide catalysts that 1) will release oxygen at temperatures lower than 1500°C (Step 2), while still maintaining water-splitting activity (Step 1) and 2) are stable up to the temperature necessary for the oxygen desorption step.

Budget: \$ 100,000

Universities: UF

Progress Summary

Several different catalysts have been fabricated and tested during several cycles using the completed reactor system described in our previous report. Iron oxide was precipitated onto three commercial zirconia supports (nanoparticle ZrO_2 , yttria stabilized zirconia (YSZ) and pellet ZrO_2), since zirconia is known as a stable material at high temperatures. These catalysts were tested for activity in the water-splitting reaction. These tests were comprised of 10 reduction-oxidation cycles, where the catalyst is first thermally activated by heating to 1500°C. This activation step produces an oxygen-deficient iron oxide, which is active in the water decomposition step. The water decomposition step reoxidizes the oxygen-deficient iron oxide to Fe_3O_4 while producing hydrogen. Each cycle therefore consists of an activation step and hydrogen production (water decomposition) step.

As zirconia is known as a material stable at high temperatures, iron was deposited onto a pellet ZrO_2 (Alfa Aesar) catalyst support and was tested for activity and stability. While the activation step generated oxygen, there was no hydrogen production from this catalyst. Additionally, the pellet zirconia was unstable and collapsed into a powder at some point during cycling. This is thus not a suitable support in this reaction.

Iron catalysts supported on nanoparticle zirconia and yttria-stabilized zirconia were therefore prepared and tested for activity. The oxygen evolution during selected activation steps is shown in Figure 1 for these catalysts. The sharp oxygen evolution peak at temperatures below 1500°C during the first activation step is due to oxygen evolution from Fe_2O_3 on the fresh catalyst, rather than from Fe_3O_4 which is present

after the water decomposition step. After the first activation step, the oxygen evolution is fairly constant for the 10 wt% iron on yttria-stabilized zirconia, while the iron on pure zirconia shows a slight decrease in oxygen evolution also after the second cycle. The oxygen evolution from the 20 wt% iron loading is shown to be significantly smaller compared to the catalysts 10 wt% iron loading. This indicates that higher iron loadings are not beneficial in this reaction.

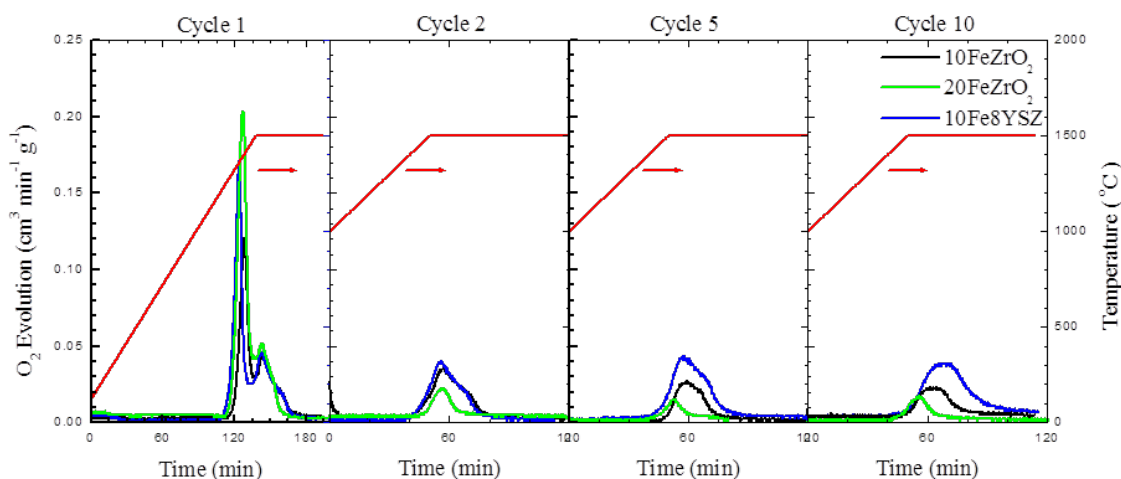


Figure 4: Activation step for cycles 1, 2, 5, and 10.

The hydrogen production steps, which follow each of the activation steps of Figure 1, are shown in Figure 2 for the same catalysts. The 10wt% Fe precipitated onto an 8% YSZ support is consistently the most productive catalyst over the 10 cycles, as the hydrogen evolution from this catalyst is higher than that of the other catalysts tested. However, the amount of hydrogen released during each cycle decreases with increasing number of cycles. In contrast, the hydrogen evolution from the 10wt% iron precipitated onto n-ZrO₂ is almost constant after the first three or four cycles. After 10 cycles, the hydrogen evolution from the iron on the yttria-stabilized zirconia is therefore close to that of the iron on zirconia. As expected from the oxygen evolution data, the 20wt% Fe loading on ZrO₂ has an inferior performance compared to the catalysts with a 10wt% Fe loading, and after 10 cycles the hydrogen evolution from this catalyst is very low.

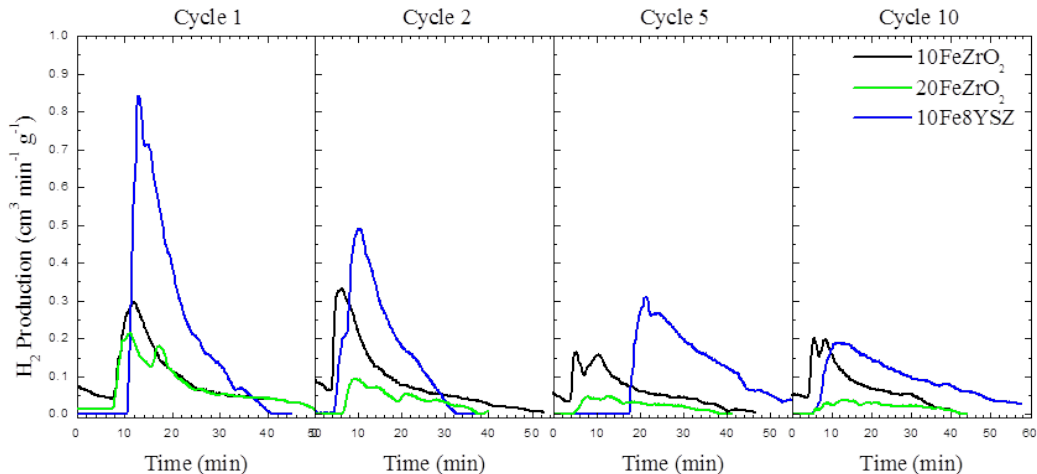


Figure 2: Hydrogen production step for cycles 1, 2, 5, and 10.

While sintering, i.e. particle growth, is observed on these catalysts, most of the catalysts are still in powder form after the 10 consecutive cycles of activation and water decomposition (Figure 3).



Figure 3: Spent catalyst after 10 cycles. Left: 10wt% Fe precipitated onto n-ZrO₂ and Right: 20wt% iron precipitated onto n-ZrO₂.

The powder catalysts will be characterized using BET, XRD, XPS, SEM, and ICP to determine the degree of sintering of each catalyst and the variation within the iron oxide between the fresh and the spent catalysts. This information will provide insight into the advantage of a zirconia support and high temperature stable materials. The characterization will assist with the fabrication of foams which will be used to support these powdered iron oxide catalysts. The purpose of using high-temperature foams to support the catalysts is to introduce pores that will not sinter or collapse at the high temperatures of this reaction.