

II.1.3 Solar-Thermal Hydrogen Production Using a Metal-Oxide Based Thermochemical Water Splitting Cycle

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Objectives

- Research and develop a cost-effective $\text{Mn}_2\text{O}_3/\text{MnO}$ solar-driven thermochemical cycle through theoretical and experimental investigations.
- Develop a process flow diagram and carry out an economic analysis of the best process option.

Technical Barriers

This project addresses the following technical barriers from the High-Temperature Thermochemical, Solar-Driven Production of Hydrogen section (3.1.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (U) High-Temperature Thermochemical Technology
- (V) High-Temperature Robust Materials
- (W) Concentrated Solar Energy Capital Cost

Technical Targets

Solar-Driven High-Temperature Thermochemical Hydrogen Production:

This project is conducting fundamental studies of the manganese oxide-based thermochemical cycle. Insights gained from these studies will be applied toward

solar-driven high-temperature hydrogen production that meets the following DOE 2010 targets:

- Cost: \$10/gasoline gallon equivalent (gge) H_2
- Process Energy Efficiency: 25%

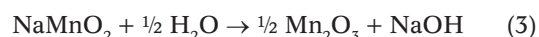
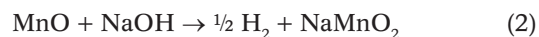
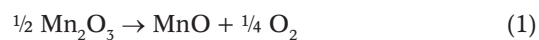
Accomplishments

- Executed a non-isothermal thermogravimetric analyzer (TGA) experimental plan to derive a reaction mechanism and initial kinetic parameters for Mn_2O_3 dissociation.
- Improved NaOH recovery by using mixed manganese oxides.



Introduction

A three-step metal oxide cycle to produce renewable hydrogen has been proposed. This cycle employs manganese oxide and solar energy to produce hydrogen [1-3]:



The $\text{Mn}_2\text{O}_3/\text{MnO}$ water splitting cycle is a three-step cycle and has advantages that make it an attractive water splitting cycle. First, Mn_2O_3 reduction occurs at low enough temperatures that feasible reactor materials of construction may be found. In addition, the “low temperatures” involved in the solar driven cycle allow for lower re-radiation losses, and in turn a higher reactor efficiency [3]. Second, an inert gas flow must be present in the metal oxide reduction of many high-temperature thermochemical cycles to thermodynamically carry out the reactions. However, the Mn_2O_3 reduction to MnO is thermodynamically favored even in the presence of air. This would eliminate the need to use inert gas to separate oxygen downstream of the reactor, which can significantly increase the overall process efficiency. Third, the phase separation of MnO from dissociated O_2 appears simple because MnO is a solid at the reaction temperature. Due to these advantages of the manganese oxide cycle it is suggested to further study the feasibility of this cycle [3-5].

Approach

TGA Mechanistic Study

A non-isothermal mechanistic study was conducted in a TGA with three factors (with selected ranges) chosen for a mechanistic investigation: (1) heating rate (9–22°C/min), (2) crucible size (20 and 100 μL), and (3) sample mass (9–36 mg). The three factors were put into a randomized central composite design, which was blocked on crucible size. Mass traces determined the extent of reaction and a mass spectrometer was used to confirm that a dissociation reaction was taking place. X-ray diffraction (XRD, $\text{CuK}(\alpha)$) was done with 2θ values between 6 and 75° on the products to confirm conversion to MnO.

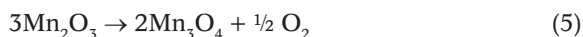
NaOH Recovery

The hydrolysis of α - NaMnO_2 in Reaction 3 requires a large excess of water for an effective separation of Mn_2O_3 from NaOH. This excess water must then be evaporated to concentrate NaOH for the hydrogen formation reaction (Reaction 2). It was hypothesized that the amount of water in the $\text{Mn}_2\text{O}_3/\text{NaOH}$ separation can be significantly reduced by replacing pure manganese oxide with a mixed metal oxide where a fraction of the manganese is replaced by other metals such as zinc or iron. The presence of the secondary metal interferes with the formation of a stable Birnessite phase that prevents efficient NaOH recovery. The NaOH recovery was investigated using two approaches: (1) A small sample of the $\text{NaOH}/\text{Fe}_x\text{Mn}_{1-x}\text{O}$ or $\text{NaOH}/\text{Zn}_x\text{Mn}_{1-x}\text{O}$ reaction products were placed in water at 80°C and the concentration of Na^+ leached from the sample was measured on-line using a conductance probe; and (2) a small sample of $\text{NaOH}/\text{Fe}_x\text{Mn}_{1-x}\text{O}$ or $\text{NaOH}/\text{Zn}_x\text{Mn}_{1-x}\text{O}$ was placed in an excess of aqueous NaOH solutions at different concentrations. After sufficient reaction times, the sample was filtered, excess solution removed by washing with small amounts of water and acetone. Reaction products were analyzed for Na^+ content, before and after water was added, and analyzed with inductively coupled plasma atomic emission spectroscopy (ICP-AES) to determine the amount of NaOH recovery.

Results

TGA Mechanistic Study

The dissociation of Mn_2O_3 in a TGA will happen in two reaction steps [6]:



It was reported in the literature that Reaction 5 will be observed in the temperature range 750°C to 1,100°C in nitrogen and Reaction 6 will be not be observed until the reaction temperature exceeds 1,400°C in nitrogen [7].

There are two regions that mass loss occurred (Figure 1), with the first region representing the transformation of Mn_2O_3 to Mn_3O_4 and the second region representing the reaction of Mn_3O_4 to MnO. Initially there was a small mass loss before the larger mass loss in the Mn_2O_3 to Mn_3O_4 transition. This was considered to be the onset of the first reaction, with a mass balance supporting this hypothesis. An in situ mass spectrometry trace demonstrated that during periods of mass loss an increase in oxygen was occurring as well. This evidence helped prove that dissociation of manganese oxide is the source of the mass loss. XRD from the end of the run confirmed that the product was MnO.

When modeling the reactions, the extent of reaction (Equation 7), α , was based on the initial mass, final mass, and mass at time t. Experimental alpha versus time values were modeled using the Arrhenius equation and a solid state mechanism $f(\alpha)$ (Equation 8). In Equation 8, β represents a constant heating rate.

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \quad (7)$$

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E_a/RT} \quad (8)$$

Both reactions of the Mn_2O_3 dissociation to MnO were modeled independently. There are different reaction mechanisms in the literature for $f(\alpha)$ and the Avrami-Erofeev mechanism (Equation 9) was found to best fit both reactions [8]:

$$f(\alpha) = n(1-\alpha) [-\ln(1-\alpha)]^{(n-1)/n} \quad (9)$$

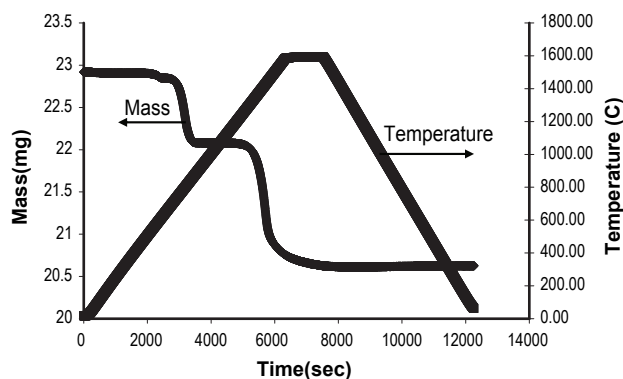


FIGURE 1. Mass Trace with Temperature Trace

The Avrami-Erofeev mechanism is considered a good model when predicting alpha values in the range of 0.15 – 0.85. Alpha versus time curves are broken down into three regions (Figure 2): (1) induction period ($0 \leq \alpha \leq 0.15$), (2) acceleratory region ($0.15 \leq \alpha \leq 0.5$) and (3) deceleratory region ($0.5 \leq \alpha \leq 0.85$). A non-linear optimization was used to find A, Ea, and n from Equations 8 and 9.

The Avrami-Erofeev mechanism modeled data from the first reaction well. However, for the second reaction, it only modeled accurately through the end of the acceleratory region. In the deceleratory region, the mechanism began to over predict alpha values. This same observation has also been reported in the literature for iron oxide dissociation [9]. Iron oxide goes through the same oxidation state changes as manganese oxide and it has been reported that the Avrami-Erofeev mechanism will accurately model that reaction through the acceleratory region as well. In the deceleratory region the authors have hypothesized that there is a diffusion resistance occurring [9]. More investigation is needed to understand what is happening in the declaratory region of the second reaction, hence kinetic values were only reported through the end of the acceleratory region for the second reaction.

Statistical tests showed that heating rate and crucible size had an effect on the activation energy for both reactions. In addition, the statistical tests indicated to a 95% confidence that the pre-exponential factor, A, and reaction order, n, are both constant. In the literature it was reported that it can be difficult to find constant, repeatable values for Ea in solid state reactions, so it was not a surprise that there is uncertainty in the values of Ea [8]. The order of reaction values, n, for both reactions are within the confidence intervals of one another. This shows that both reactions reacted the same way through the end of the acceleratory region of the second reaction.

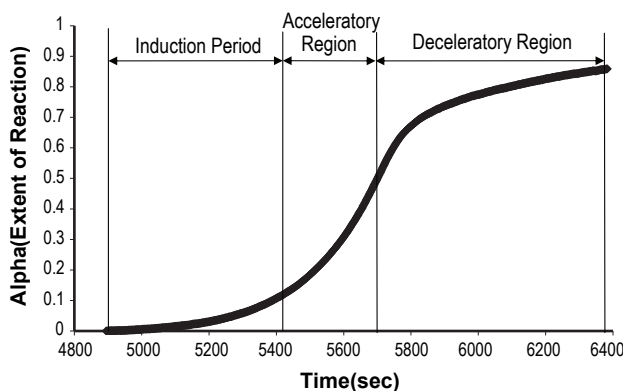


FIGURE 2. Extent of Reaction vs. Time

NaOH Recovery

Several mixed manganese oxides, with iron and zinc, at different metal:Mn ratios were synthesized using a sol-gel process. Hydrogen generation was demonstrated using mixed manganese oxides when reacted with NaOH at temperatures $>650^{\circ}\text{C}$. The change in crystal structure after the hydrogen formation was confirmed by XRD. Overall crystallinity decreased and the conversion was not complete as the pattern of the precursor was still visible.

The first method to investigate the capability of mixed manganese oxides for NaOH improvement was done using a conductance probe to measure the amount of NaOH leached from the product sample. Figure 3 compares the hydrolysis of pure NaMnO_2 and a mixed Fe/Mn compound in a 0.5 molar solution. The mixed oxide reaches steady state faster than the pure manganese sample.

The second method to test the effectiveness of NaOH recovery with mixed manganese oxides was done utilizing ICP-AES. Figure 4 compares the percentage of Na^+ leached for the pure manganese and a variety of

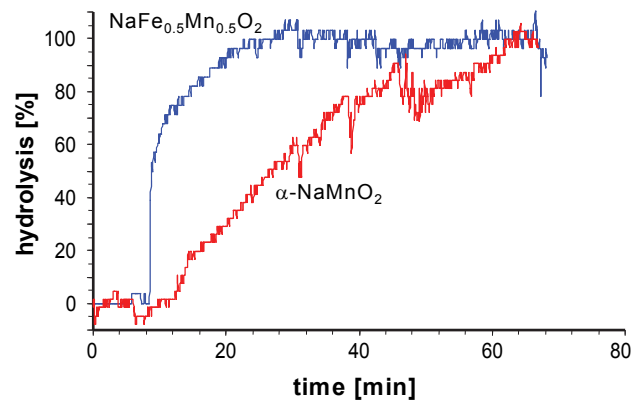


FIGURE 3. Hydrolysis of Pure NaMnO_2 and $\text{NaFe}_{0.45}\text{Mn}_{0.55}\text{O}_2$

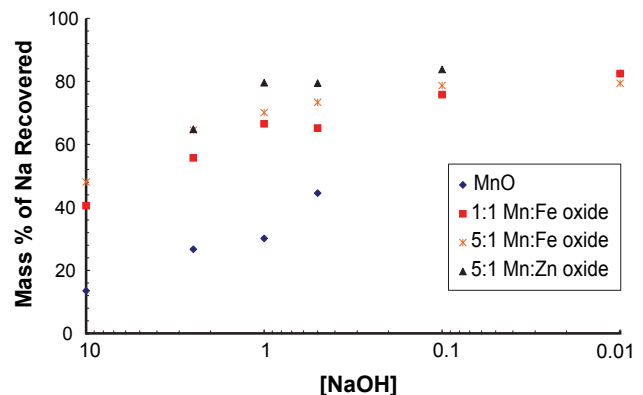


FIGURE 4. Sodium Recovery at Varying NaOH Concentrations

mixed manganese oxides. The mixed oxides released more sodium at high NaOH concentrations, than pure manganese oxide. It was found that mixed manganese oxides with zinc were the best at recovering Na⁺ at high concentrations. The results from these two studies provided evidence that the amount of water required for NaOH recovery can be significantly reduced using mixed manganese oxides.

Conclusions and Future Directions

Significant experimental progress has been made with the Mn₂O₃/MnO cycle:

- A reaction mechanism has been hypothesized for Mn₂O₃ dissociation.
- Mixed manganese oxides were shown to improve NaOH recovery.
- Experimental investigation using a mixed manganese oxide is ongoing (Mn/Zn oxide).

Future work:

- On testing of Mn₃ZnO₄ dissociation:
 - Evaluate whether reaction mechanism is similar to Mn₂O₃.
- Gain better understanding of H₂ generation with mixed manganese oxides.
- Update process flow diagram with new results to assess a Mn₂ZnO₄/Mn₂ZnO₃ cycle.

FY 2008 Publications/Presentations

1. Todd M. Francis, Casey S. Carney, Paul R. Lichty, Roger Rennels, and Alan W. Weimer, "The Rapid Dissociation Of Manganese Oxide To Produce Solar Hydrogen," Annual Meeting of the American Institute of Chemical Engineers, Salt Lake City, UT (Nov 2007).
2. Oliver J. Kilbury, Casey S. Carney, Hans Funke and Alan W. Weimer, "Improving Sodium Recovery in the Hydrolysis Step of a Manganese-Oxide Thermochemical Cycle for Hydrogen Production," Annual Meeting of the American Institute of Chemical Engineers, Salt Lake City, UT (Nov 2007)
3. Todd M. Francis, Casey S. Carney, Paul R. Lichty, Roger Rennels, and Alan W. Weimer, "The Rapid Dissociation of Manganese Oxide to Produce Hydrogen," SolarPACES 14th Biennial Symposium, Las Vegas, NV (Mar 2008).

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