

II.J.4 NHI Catalyst and Membrane Studies for Thermochemical Cycles at INL

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Objectives

- Develop enabling technologies for the Sulfur-Iodine (S-I) thermochemical cycle as a part of the Nuclear Hydrogen Initiative (NHI).
- Apply these technologies to the Hybrid Sulfur (HyS) cycle and to other non-sulfur-based thermochemical cycles.
- Technologies include effective catalysts for chemical conversions and membranes for chemical separations. These enabling technologies are needed to reduce cost and increase efficiency of the processes.

Accomplishments

- Pt/TiO₂ has shown the best wide temperature range catalytic activity and stability for H₂SO₄ decomposition.
- A commercial activated carbon, designed as a catalyst carrier, was found to be active and stable for hydriodic acid (HI) decomposition in one week of continuous testing.
- The above catalysts were recommended for the S-I Integrated Laboratory Scale (ILS) project.
- Data has been collected that will allow for determination of the applicability of pervaporation separation processes to the S-I cycle.
- The accomplishments of this project have directly addressed all project milestones and have provided a chemical separation capability for potential inclusion in the S-I ILS demonstration.
- We have continued to characterize membrane performance for process parameters necessary to model membrane system performance under

actual operating conditions – this is important to determining whether pilot-plant scale systems should be constructed and tested.

- Membrane performance for concentration of both HI and sulfuric acid are commercially competitive.
- No membrane degradation has been observed suggesting a long operational lifetime under S-I cycle conditions.



Introduction

Thermochemical cycles are proposed for the production of hydrogen by splitting water using chemical processes and energy, most preferably from a source that does not emit carbon, such as solar or nuclear energy. Efforts at the Idaho National Laboratory (INL) have not concentrated on the direct development of any particular thermochemical cycle. Rather, enabling efforts have been conducted to increase efficiency in established thermochemical cycles. In particular, the INL has focused in the sulfur family of thermochemical cycles, most advanced of which are the S-I and HyS cycles. Efforts at INL concentrate on two major thrusts: catalysts and membrane separations. Catalyst research is on-going for both the sulfuric acid and HI decomposition processes and is a significant issue due to the equilibrium-limited nature of these reactions. For the sulfuric acid decomposition process, precious metal catalysts have been the most efficient; however, catalyst deactivation is a significant problem. HI decomposition catalysts historically have been simple activated carbons.

Chemical separations also have been identified as targets for research. Specifically, we have sought to develop membrane-based separation systems for HI and sulfuric acid concentration. We have explored membranes for the removal of water from a mixture of HI, iodine, and water at temperatures between 120-150°C. Additionally, we have concentrated sulfuric acid at sub-boiling temperatures (100-120°C). The following sections of this report are divided into two parts: 1) Catalysts, and 2) Membranes.

Catalysts

Approach

The S-I cycle requires catalysts for both the H₂SO₄ and the HI decomposition reactions to achieve desired reaction rates at feasible temperatures. The goal of

this effort is to identify or develop highly active, stable catalysts for the S-I cycle. This presents significant challenges since the S-I decomposition reactions present harsh environments for catalysts. Catalysts explored for sulfuric acid decomposition included supported platinum group metals (PGMs) and complex metal oxides. HI decomposition catalyst studies focused on activated carbons.

Results

Our previous work found that platinum supported on titania (Pt/TiO₂) was a promising catalyst for the high-temperature sulfuric acid decomposition reaction. These tests were run for up to 24 hours at temperatures from 800 to 850°C. Longer term testing of up to ten days of continuous operation demonstrated that the Pt/TiO₂ catalyst deactivated due to platinum sintering, oxidation and volatilization. Efforts in FY 2007 focused on testing alternate PGM catalysts and bimetallic PGM catalysts that could potentially provide better stability and activity for the sulfuric acid reaction. PGM-based catalysts explored included Pt, Pd, Ir, Ru, and Rh, all supported on TiO₂. As shown in Figure 1, platinum and palladium had the highest initial activity but also had the highest deactivation rate (Figure 2). In contrast, Ir, Ru and Rh were very stable but displayed only low activity. At the end of 72 hours of testing, it was found that the Pt-based catalyst maintained the highest end of run activity.

Since platinum was promising, bimetallic Pt-PGM-based catalysts were tested. Bimetallic catalysts tested included Pt-Pd, Pt-Ir, Pt-Rh, Pt-Ru. Tests performed at 850°C for 72 hours showed that the Pt-Pd catalyst had the highest end-of-run activity of the bimetallic

materials. However, that end-of-run activity was only slightly higher than the activity for the Pt and the Pd mono-metallic samples. Further tests were conducted with the Pt, Pd and Pt-Pd catalyst over a temperature range from 750 to 850°C. Results showed that the Pt-based catalyst had superior performance over the other two catalysts. Thus, Pt is the preferred catalytic metal for the decomposition of sulfuric acid; however, improved stability is still required.

Activated carbon samples were explored for the HI decomposition reaction. Two sets of samples were studied; an academic set supplied by the University of San Juan, Argentina, and commercial activated carbons from Carbon Activated Inc. and NORIT Americas Inc. It was found that there was a large variation in activity and stability for the HI decomposition reaction among the activated carbon samples. For the academic carbons, activity, based on hydrogen yield, was found to be greatest when the fraction of mesoporous surface area was greatest, ash content was low (<10%) and total acid sites were high (>50 meq/100 g). Of the commercial catalysts, the NORIT RX 1.5 EXTRA material was found to have among the best activity and high stability.

Membranes

Approach

Within the S-I cycle, there are numerous chemical separations that may be possible to perform using membranes. This aspect of the INL effort has concentrated on the development of pervaporation

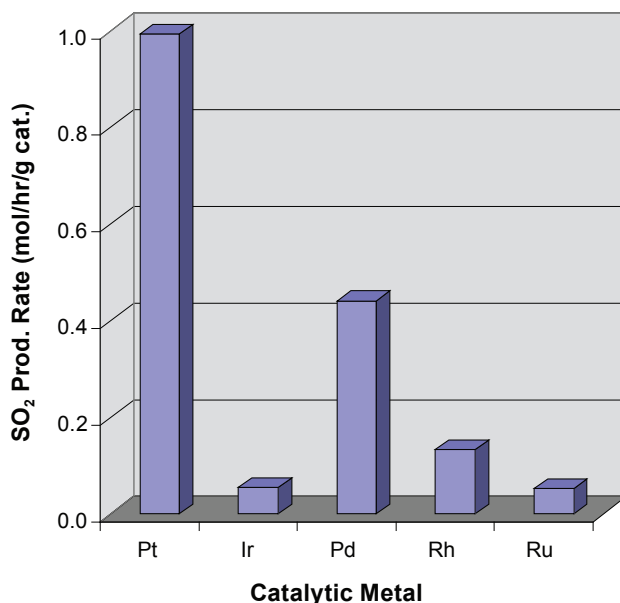


FIGURE 1. Initial SO₂ Production Rate at 850°C

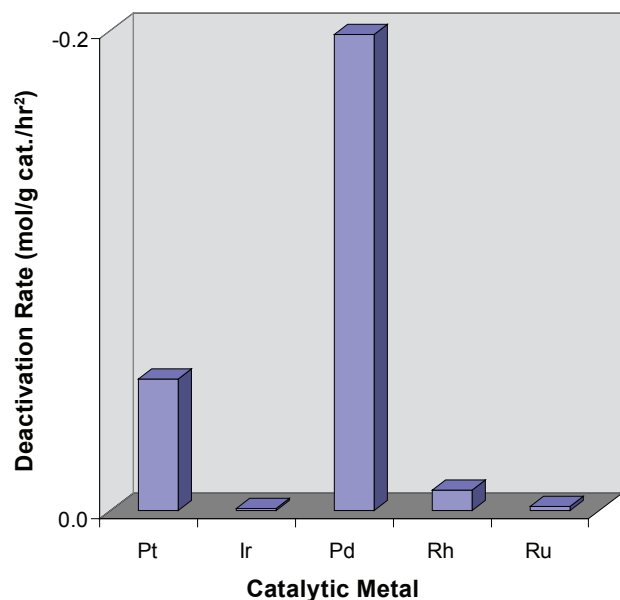


FIGURE 2. Initial Deactivation Rate at 850°C

technology for the concentration of HI/iodine and H_2SO_4 feedstreams at temperatures between 100 and 140°C. Pervaporation is a technique where the feed is exposed to the membrane at little to no pressure. Membranes that are selective for the desired permeant are used and the driving force for the separation is removal of permeants from the membrane backside. For this work, Nafion[®] membranes have been found to be highly selective for water over either acid with no observed membrane degradation.

Results

We have demonstrated that membranes can be employed for the concentration of both HI (and HI/iodine) and sulfuric acid. Membrane performance is shown in Figures 3 and 4 where plots are included

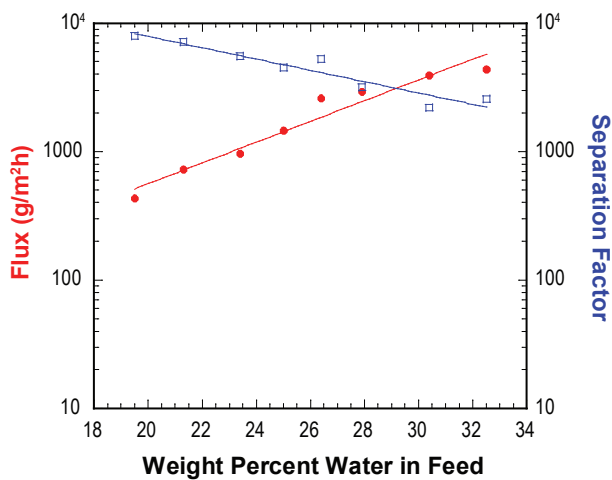


FIGURE 3. Performance Data for Nafion[®]-112 Membrane Against a HI/Iodine Feed

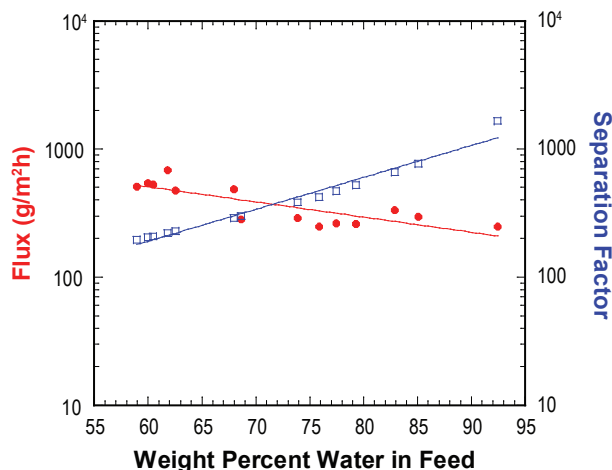


FIGURE 4. Sulfuric Acid Concentration Data Using a Nafion[®]-112 Membrane

for both flux of water through the membrane and the separation factor, which is a measurement of how well the membrane performs the separation. Figure 3 shows the data for an HI/iodine/water experiment using a 50 μm thick Nafion[®]-112 membrane at 134°C. The water flux is proportional to the concentration of water in the feed and inversely proportional to the separation factor. This is a commonly observed behavior in membrane science termed the permeability/selectivity trade-off. Water fluxes range from 400 to 4,000 g/m^2h while the separation factor varied between 2,000-8,000. Both of these values are commercially competitive and no degradation of the membrane occurred.

Considering the performance of Nafion[®] membranes for concentration of HI, it was proposed that sulfuric acid could be concentrated as well. Figure 4 shows the performance of a Nafion[®]-112 membrane for the concentration of sulfuric acid from 58% to 92%. Water fluxes ranged from 200-800 g/m^2h and the separation factors varied from 200 to 1,000, depending on acid concentration in the feed. These values represent commercially attractive performance. Sulfuric acid posed one additional factor that had to be considered. Chemically, HI is mainly corrosive and materials had to be chosen with this fact in mind. Sulfuric acid, in addition to being corrosive, is a strong oxidizer. Upon visual inspection of the membranes after use, no degradation was observed. Instrumental studies are underway to verify this conclusion.

Conclusions and Future Directions

These projects are providing the enabling science and technology to make the S-I thermochemical cycle driven by nuclear energy an efficient reality. Laboratory-scale systems have been employed to characterize catalyst and membrane function. Pt/TiO₂ was found to be an acceptable catalyst for the sulfuric acid decomposition reaction, while HI can be decomposed over relatively stable activated carbon catalysts. Nafion[®] membranes have been determined to be highly selective for water from both HI and sulfuric acid and are highly durable under extreme process conditions. Further, membranes have been identified for both H₂/HI/I₂ and SO₂/O₂ separations. Future work for these projects includes the development of catalysts with increased stability and low-temperature activity for economic, long-term H₂ production by the S-I cycle. For the separation effort, future work is needed to complete membrane characterization and process modeling is needed that will provide a basis of decision for inclusion of the technologies in the S-I ILS.

FY 2007 Publications/Presentations

1. D.M. Ginosar, L.M. Petkovic, A.W. Glenn, K.C. Burch, “Stability of supported platinum sulfuric acid decomposition catalysts for use in thermochemical water splitting cycles.” *International Journal of Hydrogen Energy*, 32, 482-488, 2007.
2. D.M. Ginosar, H.W. Rollins, L.M. Petkovic, K.C. Burch, M.J. Rush, “High-temperature sulfuric acid decomposition over complex metal oxide catalysts” submitted to *International Journal of Hydrogen Energy*, 2007.
3. D.M. Ginosar, L.M. Petkovic, H.W. Rollins, and K.C. Burch, “Platinum Group Metal Catalysts for Sulfur-Based Thermochemical Water Splitting Cycles.” paper 230a, American Institute of Chemical Engineers National Meeting, San Francisco, CA, November 12–17, 2006.
4. D.M. Ginosar, L.M. Petkovic, H.W. Rollins, K.C. Burch, C.Deiana, H.S. Silva, M.F. Sardella, D. Granados, “Activated Carbon Catalysts for the Production of Hydrogen via the Sulfur-Iodine Thermochemical Water Splitting Cycle” North American Catalyst Society 20th Meeting, Houston, TX, June 2007.
5. D.M. Ginosar, L.M. Petkovic, H.W. Rollins, K.C. Burch, “Catalyst Needs for Thermochemical Hydrogen Production Cycles” To be presented at Global 2007, Boise, ID, September 2007.
6. Frederick F. Stewart, Christopher J. Orme, and Michael G. Jones, “Membrane Processes for the Sulfur-Iodine Thermochemical Cycle”, *International Journal of Hydrogen Energy* 2007, 32, 457-462.
7. Christopher J. Orme and Frederick F. Stewart, “Pervaporation of Water from Aqueous Hydriodic Acid and Hydriodic Acid/Iodine Mixtures Using Nafion Membranes”, Accepted for publication in *Journal of Membrane Science*, 2007.
8. Christopher J. Orme, John R. Klaehn, and Frederick F. Stewart, “Membrane Separation Processes for the Benefit of the Sulfur-Iodine and Hybrid Sulfur Thermochemical Cycles”, Submitted to *International Journal of Hydrogen Energy*, 2007.
9. Frederick F. Stewart and Christopher J. Orme, “Advances in Acid Concentration Membrane Technology for the Sulfur-Iodine Thermochemical Cycle” Presented to the Annual AIChE Meeting, Nuclear Engineering Division, San Francisco, CA, November 2006.