CATALYTIC REACTOR PERFORMANCE OF A BOROHYDRIDE HYDROGEN GENERATOR

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Introduction

Hydrogen storage is one of the most important issues and potentially the biggest technical barrier to the implementation of a hydrogen economy. Both physical and chemical storage methods are under investigation in order to solve this challenging technical problem. Among all the options, hydrogen storage systems based on chemical hydrides[1,2] have demonstrated gravimetric and volumetric hydrogen storage densities that meet the near term targets and approach the long-term targets of the FreedomCar Initiative. Particularly, sodium borohydride ($NaBH_4$) based systems[3] have shown impressive system performance characteristics.

Sodium Borohydride reacts with water to generate high purity humidified hydrogen gas (H_2) (Eq. 1) suitable for use in proton exchange membrane (PEM) fuel cells. This hydrolysis reaction takes place spontaneously in an un-stabilized solution, and the reaction rate increases dramatically with temperature. Addition of a base such as NaOH or KOH to aqueous solutions of $NaBH_4$ can stabilize the solution against hydrolysis, but the reaction can be initiated again with a suitable catalyst. It is this catalyzed hydrolysis that forms the basis of the Hydrogen on Demand™ (HOD™) technology.

$$NaBH_4 + 4\ H_2O = NaB(OH)_4 + 4\ H_2\uparrow \qquad (1)$$

An effective catalyst is critical to quantitatively and controllably extracting the hydrogen stored in mixtures of borohydride and water. One of the first reports on the catalyzed hydrolysis by Brown[4] examined a number of metals and established relative rates for hydrogen generation using these catalysts. According to Brown, noble metals such as ruthenium (Ru) and rhodium (Rh) are excellent catalysts for this reaction. More recently, less costly metal-boron alloys such as nickel boride and cobalt boride are also reported to be effective catalysts.[5,6]

The desired catalyst has to offer superior reactivity to ensure fast hydrogen generation. High conversion of $NaBH_4$ to H_2 is critical. It is desirable that the catalyst is capable of operating with high concentration $NaBH_4$ fuel over a wide range of fuel throughput (or space velocity). The catalyst also needs to provide fast start-up and be sufficiently durable. Optimization of reactor throughput will result in reduction of catalyst chamber volume and weight, thereby reducing the balance of plant (BOP) in the hydrogen storage system and increase overall gravimetric and volumetric storage efficiencies.

Many factors influence the activity and reactor performance of a catalyst, such as catalyst preparation procedures, catalyst support materials, chemical and morphological transformations of the catalyst surface during reaction, as well as reactor design, operating conditions, and heat and mass transfer issues. To understand the catalyst system, each of these factors should be isolated and studied in detail to the extent possible. In this paper, we report preliminary reactor performance results on a few critical parameters, which include %$NaBH_4$ conversion, liquid feed space velocity, and catalyst durability, of the HOD™ catalysts in a packed bed reactor operating under various hydrogen flow conditions. Results from these studies provide information and direction for further improvements in the catalyst technology.

Experimental

Catalyst Preparation and Fuel Composition The active metal catalyst was supported on a suitable metallic substrate according to methods taught in U.S. Patent 6,534,033 B1[7]. Two catalysts, BMR05 and BMR06, which contain different loadings of active catalyst were selected for detailed evaluation. The fuel solution used in the experiments typically contains 20 wt% $NaBH_4$.

Measurements of Hydrogen Generation Catalyst activity is measured by the apparent hydrogen evolution rates. In many previous reports, hydrogen generation rates were measured from batch type reactors, where a specific amount of catalyst is placed in stagnant or stirring borohydride solution and the resultant hydrogen generation rates measured. In such a configuration, the product sodium metaborate ($NaB(OH)_4$) is mixed with reactant $NaBH_4$ in the same solution, and it is often difficult to achieve close to quantitative conversion of $NaBH_4$ without providing external heating to the solution.

In the results reported below, all hydrogen generation rates were measured using a flow reactor. In a typical experiment, a cylindrical reactor of certain volume is packed with a constant amount of catalyst for testing. One end of the reactor is connected to a fuel line via a metering pump. The rate of liquid flow into the reactor is monitored by the weight change of the fuel reservoir. The other end of the reactor is connected to a liquid-gas separator where hydrogen gas and the liquid by-product, $NaB(OH)_4$ solution, are separated. In the flow reactor, metaborate does not back mix with the $NaBH_4$ reactant solution. The separated hydrogen stream then passes through a condenser and a drying column to remove water and ensure accurate measurement of hydrogen flow rate. Conversion of borohydride to hydrogen, or reaction yield, is calculated by dividing the measured hydrogen flow rate by the theoretical hydrogen flow rate calculated based on the fuel feed rate.

Catalyst Durability Data were collected from semi-continuous operation. The reactor was operated at a constant liquid feed space velocity for 6-8 hours a day. At the end of the day, reactor was shut down and catalyst bed rinsed with water. The next day, same procedures were repeated, and on-stream hours accumulated.

Results and Discussion

Conversion Efficiency and Throughput Sodium borohydride conversion efficiency was measured over a range of fuel flow rates. One of the advantages of borohydride hydrolysis is that the reaction

can go to 100% completion with no side reactions. The challenge in a flow reactor is to maximize the fuel throughput rate while preserving 100% conversion of the reactant. The higher the throughput, the smaller the reactor volume required for a given hydrogen output level. Figure 1 shows typical experimental conversion results. It can be easily seen from the graph that for space velocity up to ~1.25 min^{-1} (or 75 hr^{-1}), conversion of borohydride to hydrogen remains above 95%.

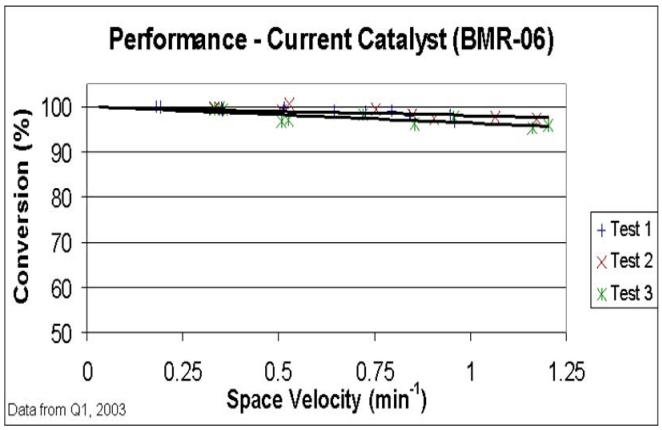

Figure 1. Conversion of $NaBH_4$ at various liquid feed space velocity.

Durability Durability of the catalyst was measured to ensure that there is no drastic deactivation of catalyst. Figure 2 depicts a durability study of catalyst BMR05. Constant performance level was demonstrated for more than 400 hours of run time. Hydrogen generation rate remained relatively constant, about 8.1 SL/min, at a constant liquid fuel feed rate of 18 g/min, corresponding to ~95% $NaBH_4$ conversion throughout the experiment. The three thermocouples evenly spaced along the reactor length recorded steady temperatures between 140-150°C. In a separate durability test

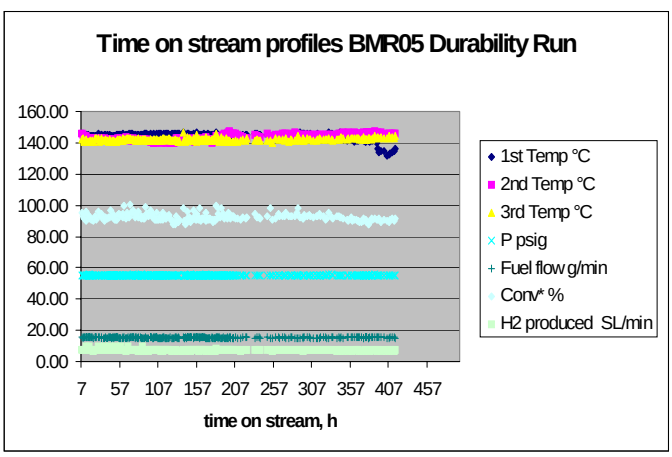

Figure 2. Time on Stream Profile of BMR05. Sodium borohydride conversion, hydrogen flow rate, fuel flow rate, system pressure, and reactor temperatures are plotted as a function of time on stream.

of catalyst BMR06 (based on a slightly modified recipe), more than 700 hours of run time has been accumulated and no significant drop in performance level has been observed. In both experiments, the liquid feed space velocity was maintained at 0.25 min^{-1} (or 15 hr^{-1}), and the system pressure was regulated at 55 psig.

Additional data also indicate that durability of the catalyst varies with different catalyst supports. In some cases, only a few days of high conversion operation was sustained before the catalyst became ineffective. Furthermore, catalyst durability often decreased with increasing liquid feed space velocity. More extended durability studies will be carried out as catalyst preparation procedures and materials properties are optimized. We expect to be able to demonstrate catalyst durability on the order of several thousand hours.

Conclusions

Higher sodium borohydride conversion can be achieved over a wide range of fuel feed space velocity in a packed bed flow reactor system. The reaction is self-sustaining, without need for external heating to achieve higher % conversion. Initial durability studies indicated that the current generation of catalyst can be operated for more than 700 hours on stream without significant loss in activity. Further improvements can be made on durability by optimizing catalyst preparation procedures and reactor engineering.

Overall optimization of the catalyst will depend on our increased understanding of the catalyst composition, structure, as well as reactor operation conditions.

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