Evaluation of Hydrogen-Oxygen Recombiner Catalysts Under Various Conditions for Nuclear and Non-Nuclear Hydrogen Safety

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Abstract

Hydrogen plays an important role in nuclear and non-nuclear safety, as the unsafe manipulation of hydrogen can lead to dangerous accidents. This concern has led the Hydrogen Isotopes Technology Branch at the Canadian Nuclear Laboratories to develop catalysts in order to aid in the recombination of hydrogen and oxygen. This research project evaluates catalysts with different compositions under various conditions (i.e. dry, humid) in a spinning basket reactor (SBR). Results suggest that catalysts with lower wetproof coating loading have higher activity levels after being exposed to water vapour or immersed in liquid water compared to catalysts with higher amounts of wetproof coating. The specific activity levels were $1.91 \text{ cm}^3 \text{ H}_2/\text{s-gCAT}$ and $1.57 \text{ cm}^3 \text{ H}_2/\text{s-gCAT}$, normalized to the benchmark catalyst's activity in humid conditions, for catalysts with low and high amounts of wetproof coating, respectively.

Normalization was performed so that the activity levels of the benchmark catalyst in humid conditions was equal to one, thus assigning the other activity level values based on their relation to the benchmark catalyst's activity levels in humid conditions. For the benchmark catalyst, activity levels in water vapour and immersion conditions were about the same, whereas activity levels for the newly developed catalysts (with low and high wetproofing agent loadings) varied depending on the water exposure levels of the test. Thus, despite the wetproofing, the amount of water exposure had an effect on catalyst activity levels. This trend demonstrates that the benchmark catalyst was well wetproofed and suggests that further improvement is needed in the wetproofing method used for the new catalyst.

Key Words

Spinning Basket Reactor (SBR), wetproofing, catalysts, hydrogen, recombinder

Introduction

A catalyst is a material that speeds up the rate of a chemical reaction by lowering the activation energy required to start the reaction. The catalysts used in this experiment were all composed of three main parts - a support, an active component, and a promoter (1). In the very centre of the catalyst is the catalyst carrier, which is surrounded by the active component: platinum supported on a high surface area material. On the outermost layer is the wetproof coating. The purpose of the wetproof coating is to prevent water from condensing in the pores. If water were to condense in the pores, the catalyst would be deactivated due to the reduction in the number of active sites that can be utilized in reactions.

The main purpose of this project is to test the Canadian Nuclear Laboratories' (CNL) new wetproofed catalysts, under harsh conditions, in order to find a catalyst that is effectively wetproofed and shows desired activity levels for different recombinder designs. Wetproofing is accomplished by applying a chemical layer to the outside of a catalyst in order to prevent liquids from entering through the pores. In this experiment, "harshness" refers to the amount of water exposure (e.g. running steam over the catalyst is less harsh than submerging the catalyst in deionized water). Four different catalyst batches were tested, including a benchmark catalyst. Benchmark catalysts have been used by CNL for many years and have been proven to be effective and efficient. However, its availability is currently uncertain due to increased difficulty in obtaining the raw materials to produce the catalyst. The benchmark catalyst uses a support made of hydrophobic silica, different from the current catalysts. This research will assist in determining which batch of catalysts are effective. In the future, these catalysts may be implemented in various hydrogen safety devices or heavy water and tritium production practices, such as a trickle bed recombinder (TBR). Recombiner catalysts such as these are implemented near hydrogen abundant areas (i.e. near a nuclear reactor) so as to reduce the risk of hydrogen-induced explosions. This is accomplished by deducting the amount of hydrogen present in the air when reacting it with oxygen to form water.

Materials and Methods

Spinning Basket Reactor. There are many different components to the SBR, as shown by Figure 1. The SBR used was comprised of hydrogen and oxygen gas valves, a humidifier, a Carberry-type reactor vessel, an ice water bath, and a drying tube, along with a gas chromatograph attached to the end of the drying tube. The way the rig functioned is as follows.

Air and hydrogen flow through the machine in set amounts, which then congregated at the reactor vessel where the mixture reacted with the catalyst, while being spun at a high speed (i.e. 1500 rpm). The basket was spun to increase mass transfer for the reaction. After the hydrogen and oxygen recombined in the reactor vessel, the newly formed product, water, traveled down to the water vapour trap and then passed through a drying column to be removed before the sample gas entered the gas chromatograph.

Recombination Rate. For this particular experiment, the recombination rate was used to measure the input and output concentrations of hydrogen gas. The recombination rate is the rate at which hydrogen gas and oxygen gas combine together to form water. This

rate helps determine the efficiency of the catalyst and was calculated using the following equation:

$$r = \frac{V_t}{60} \times \Delta ppm \times 10^{-6} \frac{1}{m}$$

where r is the recombination rate in $\text{cm}^3 \text{H}_2/\text{s-gCAT}$, V_t is the total flow through the reactor in mL/min , Δppm is the average H_2 inlet concentration minus the average H_2 outlet concentration, and m is the mass of the catalyst in grams. The total flow rate is divided by 60 in order to convert the total flow in seconds, rather than minutes, and concentration was multiplied by 10^{-6} , for ease of comparison.

Testing The Catalyst With 0% Humidity (Dry Test). The SBR setup is shown in Figure 1. The catalysts were first weighed to the proper amount before being distributed evenly among each section of the basket. A pressure test was then conducted on the rig to check for any system leaks. Afterwards, the airflow was set to 1.16 psi and hydrogen flow was set to the desired amount. The motor was set to 1500 rpm, then checked using an Omega Tachometer - Model HHT13, and the sample loop pressure was set to 785 mmHg. Outlet and inlet gas concentrations were measured using an Agilent Tech-

Figure 1: A schematic of the spinning basket reactor (SBR). The SBR was designed by the Hydrogen Isotopes Technology branch at CNL and then built by Renaud Tremblay.

nologies Gas Chromatograph 6890N Network GC System with a GC Chemstation and a Cole Parmer Flow Meter - Model 32908-71 was used to measure flow rate.

Testing The Catalyst Under Humid Conditions (Water Vapour).

The procedure is similar to the dry test, with the exception of turning on the humidifier after setting the motor speed and prior to setting the sample loop pressure.

Testing The Catalyst Under Humid Conditions (Exposure to humid gas without hydrogen). The procedure is similar to the dry test, with the exception of turning on the humidifier and running steam through the catalysts for one hour, before setting the sample loop pressure and analyzing gas concentrations.

Testing The Catalyst Under Wet Conditions (Immersion in deionized water). After weighing and loading the catalysts in the basket, a beaker was filled with enough deionized water to fully submerge the basket. The catalyst basket was then placed in the beaker for precisely one hour, before being removed and placed into the SBR. The test then followed the humid water vapour condition tests.

Results and Discussion

Past test results from CNL had shown that the catalysts produced with the high platinum and high support loading with either high or low wetproof loading had some of the highest activity levels (3). It was thought that because their activity levels were so high, a drop in activity would be more noticeable, as opposed to the lower activity catalysts. Levels that are four times greater than the benchmark catalyst's rate in humid conditions are considered high, while levels equal to or less than the benchmark catalyst's rate in humid conditions are considered low.

There were four different catalysts tested – the benchmark catalyst, the catalyst with no wetproofing agent, and the low and high catalyst formulations. All of the catalysts, with the exception of the benchmark, had the same amount of platinum and support loading but different amounts of wetproofing agent. Formulation_{low} had low amounts of wetproofing agent compared to formulation_{high}. Formulation_{high} and the benchmark catalyst had similar weight percentages of the wetproofing material. The catalysts with low amounts of wetproofing agent had less of the wetproofing material applied during the creation of the catalysts than the catalysts with high amounts of wetproofing agent.

Figure 6: The activity levels of the four catalysts in various experimental conditions.

In Figure 2, all data points have been normalized to the benchmark catalyst's activity in humid conditions.

The results of the experiments were very promising but some of the data collected was contradictory, as shown in Figure 2. The catalyst with no wetproofing agent was deactivated in the humid condition, thus sequence and immersion tests were not implemented. Furthermore, its activity under dry conditions was also marginal; its levels were 3.5% of the low wetproofed catalyst's levels and only about 4% of the high wetproofed catalyst's levels. It appeared that the wetproofing agent indeed had an effect on the efficiency of the catalysts, even in dry conditions, although the rationale for this is still unknown. It is possible that this was due to the added chemical composition of the wetproofing agent on top of the catalysts' composition.

Generally, the formulation_{low} catalyst demonstrated higher activity levels than the formulation_{high} catalyst, except when exposed to humid air. In the exposure to humid air condition, the formulation_{high} catalyst produced a recombination rate of 5.88 cm³ H₂/s·gCAT while the formulation_{low} catalyst produced a rate of 4.68 cm³ H₂/s·gCAT (normalized to the benchmark catalyst's levels in humid conditions).

The formulation_{high} catalyst proved to have very high activity levels in all conditions, but unexpectedly, the low wetproofed catalyst had even higher activity levels. This is unusual, as it was expected that the higher amount of wetproofing agent a catalyst had, the higher the activity and the better protected it would be in humid conditions. However, this data may be unreliable as only one test was done so a standard deviation was not produced.

The immersion tests proved to be the harshest condition, as it cut down the activity levels the most. For the benchmark catalyst, the activity in immersion was about 35% of the dry conditions activity level. For formulation low and high catalysts, the immersion levels were only about 10% each, which was unexpected given that the two catalysts contained different amounts of wetproofing material. The benchmark catalyst and the new catalysts were wetproofed using different methods. It can thus be concluded that the benchmark catalyst's wetproofing method is more effective.

It should be noted that most of the catalysts were only tested once, so the standard deviation could not be estimated. Therefore, the confidence in accuracy of the measurements cannot be high. Future studies should replicate this experiment with similar conditions and catalysts to determine whether or not the data is consistent and accurate.

It is clear that the new catalysts show high activity levels but it is unclear as to how well wetproofed they are. The benchmark catalyst was very well wetproofed as its activity levels in humid conditions (i.e. humid gas without hydrogen or immersion in water) were very

similar, while the new catalysts' levels gradually sank as the intensity of the exposure to water tests increased. In addition, it was unexpected to note that the catalyst with the low wetproof coating had higher activity levels under water vapour or immersion in water than the catalyst with the high wetproof coating, though this cannot be definitely concluded until a standard deviation is derived. Nevertheless, the difference tends to be small and may be explained by the error associated with the experiments themselves.

Conclusion

In the end, the catalyst that is found to be the most efficient will be placed into a TBR for lifetime testing. If the catalyst is still found to be effective at the end of that testing, it will likely undergo a testing with deuterium, as well as radiation exposure tests. Past results from CNL have shown that a higher amount of radiation does affect the activity levels of catalysts over time (2). If this catalyst were ever to be used with tritium or near other radiation sources, knowing its behavior in the presence of radiation would be essential. Other wetproofing methods should also be explored, as well as other coating materials more similar to that used by the benchmark catalyst.

These wetproofed catalysts allow for the recombination of hydrogen and oxygen in cool, humid conditions, rather than the heated conditions that would be required for conventional recombiners (4). This greatly mitigates the dangers associated with most catalytic recombiners (5). Should the catalysts be implanted in a recombiner, such as a passive autocatalytic recombiner (PAR), the risk of hydrogen-related incidents may greatly be reduced (3).

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REVIEW

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The author of this work presents a manuscript describing a comparative study of different catalyst mixtures for a given nuclear application. I enjoyed reading this manuscript and have some comments for the authors' consideration attached. In general, although the limitations of this study are clearly presented by the author, there seems to be a need for a more thorough description of various points in the interest of clarity and reproducibility.