HUMIDITY TOLERANT HYDROGEN-OXYGEN RECOMBINATION CATALYSTS FOR HYDROGEN SAFETY APPLICATIONS

Gardner, L., Vega, A., Tremblay, R.P., Suppiah, S. and Ryland, D.

Chemical Engineering Branch, Canadian Nuclear Laboratories, Chalk River Laboratories,
K0J 1J0, Canada, lee.gardner@cnl.ca

ABSTRACT

Catalytic hydrogen-oxygen recombination is a non-traditional method to limit hydrogen accumulation and prevent combustion in the hydrogen industry. Outside of conventional use in the nuclear power industry, this hydrogen safety technology can be applied when traditional hydrogen mitigation methods (i.e., active and natural ventilation) are not appropriate or when a back-up system is required. In many of these cases it is desirable for hydrogen to be removed without the use of power or other services, which makes catalytic hydrogen recombination attractive. Instances where catalytic recombination of hydrogen can be utilized as a stand-alone or back-up measure to prevent hydrogen accumulation include radioactive waste storage (hydrogen generated from water radiolysis or material corrosion), battery rooms, hydrogen-cooled generators, hydrogen equipment enclosures, etc.

Water tolerant hydrogen-oxygen recombiner catalysts for non-nuclear applications have been developed at Canadian Nuclear Laboratories (CNL) through a program in which catalyst materials were selected, prepared and initially tested in a spinning-basket type reactor to benchmark the catalyst's performance with respect to hydrogen recombination in dry and humid conditions. Catalysts demonstrating high activity for hydrogen recombination were then selected and tested in trickle-bed and gas phase recombiner systems to determine their performance in more typical deployment conditions. Future plans include testing of selected catalysts after exposure to specific poisons to determine the catalysts' tolerance for such poisons.

1.0 INTRODUCTION

Catalyst development has been a successful research and development area for the Hydrogen Isotopes Technology Branch at Canadian Nuclear Laboratories (CNL – formerly Atomic Energy of Canada Limited or AECL), with respect to the numerous catalysts applied in industrial applications. As a result of this success, CNL has developed significant intellectual property and capabilities in catalyst development and testing. To utilize these capabilities, efforts have been taken to exploit catalyst research through deployment outside of the traditional CNL catalyst applications (i.e., applications associated to operations of nuclear reactors or heavy water production/upgrading or tritium handling and extraction).

A thorough review of applications that are outside of the traditional fields for CNL catalysts has been carried out. From the review, one of the recommendations made was to pursue volatile organic compound (VOC) control applications using hydrogen recombiner catalysts. The focus was then narrowed to waste storage applications where hydrogen produced through radiolysis in enclosures must be removed. Such applications may also involve exposure of the catalyst to inorganic and organic contaminants.

This paper provides details on the application of hydrogen recombination catalysts to radioactive waste storage. It also discusses the catalyst testing work for this application and the plans for future demonstration of the validity of CNL catalysts for the target application.

2.0 BACKGROUND

2.1 Waste Storage

A long standing issue with the storage of radioactive waste is the potential for hydrogen generation and accumulation. The issue commonly arises from water in the waste solution breaking down into its constituents (hydrogen and oxygen), due mainly to the presence of radiation (i.e., water radiolysis). As a result of the hazardous chemicals and radioisotopes in the waste solution, direct venting of the waste storage vessel, to allow the hydrogen to escape, is not acceptable. As a result, the accumulation of hydrogen is dealt with by applying active ventilation or passive venting to the storage vessel. These systems are costly engineering projects to design and execute, and increase the complexity of the storage vessel.

2.2 Application of CNL's Hydrogen Recombiner Catalyst

Hydrogen recombiner catalyst technology can be applied to the waste storage tanks to prevent the accumulation of hydrogen from reaching flammable levels. The hydrogen recombiner catalyst removes hydrogen from the atmosphere by inducing a reaction between hydrogen and oxygen (in air) on the surface of the catalyst. The products from this reaction are heat and water vapour. An important feature of CNL hydrogen recombiner catalysts is their proprietary wetproofing, which allows them to function in high humidity (up to 100% relative humidity (RH)) and low temperature (10 °C) environments, expanding the operating envelope of the catalysts.

For this application of CNL hydrogen recombiner catalyst, it is expected that a small amount of catalyst material could be positioned in the vessel in a structure that would support the catalyst material (without degrading) in the tank headspace environment, and would allow for the gas in the tank headspace to freely contact the surface of the catalyst. The catalyst would maintain the hydrogen concentration in the tank headspace below flammability levels, thereby eliminating the need to vent the tank headspace atmosphere. The heat generated from the exothermic recombination reaction is not expected to impact the waste storage system due to the large quantity of waste in the tank, and the lack of insulation on the tank.

In order to determine the validity of hydrogen recombiner catalysts for this application, tests must be conducted with candidate CNL catalysts. To closely simulate the application, a test would be performed in a representative atmosphere (i.e., temperature, pressure and humidity) with selected contaminants expected in the headspace of the tank.

2.3 Expected Waste Storage Tank Conditions and Contaminants

A wide variety of contaminants in waste tank head space has been identified in the literature. Further, the range of concentrations of the contaminants reported is also significant. However, the trapped gases in the waste tank headspace were found to be predominantly hydrogen, nitrous oxide and ammonia [1].

Waste tank headspace conditions were found to vary with ambient conditions. Tank headspace temperatures were found to range from 16 to 61 °C [2]. Since the tanks are vented, the headspace pressure is often close to ambient pressure. Quantitative values of the humidity of waste tank headspace were not found in the available literature; however, more qualitative values were found, suggesting that the humidity in a tank headspace will vary closely with ambient conditions [1].

2.4 CNL's Wetproofed Hydrogen Recombiner Catalysts

Over the past 15 – 20 years, CNL's hydrogen recombiner catalysts have been successfully implemented in several different applications.

- The passive autocatalytic recombiner (PAR), currently licensed by Candu Energy Inc., utilizes CNL's recombiner catalysts. The PAR has undergone extensive qualification testing for installation in nuclear containment buildings to mitigate hydrogen in the event of a nuclear accident [3].

- Hydrogen recombination is employed to purify hydrogen, typically when the hydrogen is produced through electrolysis. During electrolysis, some oxygen crosses over and contaminates the hydrogen stream. The oxygen is removed by passing the product gas over a hydrogen recombiner catalyst. The resulting water vapour is then easily removed in a drying system.

- In heavy water upgrading or production, or tritium removal processes, hydrogen (or deuterium or tritium) is recombined to water vapour by passing the gas over a bed of catalyst (with or without a flow of water to cool the catalyst bed) [4].

From the need of the various applications, CNL's hydrogen recombiner catalysts have had numerous formulations that have a range of beneficial features. New catalyst formulations are being developed to expand the capabilities and versatility of CNL's hydrogen recombiner catalysts, particularly under conditions where volatile organic compounds (VOCs) are present.

3.0 PRELIMINARY CATALYST TESTING

Initial testing was performed to screen catalyst formulations and determine what catalysts were appropriate to conduct application specific testing. The preliminary testing was conducted in a system that quickly yields results (~2 hours) on catalyst performance for hydrogen recombination.

After numerous preliminary tests, several different catalysts, some of which that have been successfully implemented in various applications, were selected as candidate materials for testing to determine their applicability for use in a waste storage environment. The catalysts and details regarding their relative properties are provided in Table 1.

Table 1. Comparison of batches of catalyst tested.

Catalyst Formulation	Structure	Catalyst Support	Active Metal	Active Metal Concentration*	Wetproofing Agent Concentration*
CatA **(baseline catalyst)**	6 mm spheres	SiO_2	Pt	1.0	1.0
CatB	6 mm spheres	TiO_2	Pt	0.8	0.5
CatC	6 mm spheres	TiO_2	Pt	0.7	1.1
CatD	6 mm rings	TiO_2	Pt	0.8	0.5
CatE	6 mm rings	Carbon	Pt	1.6	0.3

*(Note: active metal and wetproofing agent concentration values are normalized to the baseline catalyst)

3.1 Spinning Basket Reactor (SBR) System

A Spinning Basket Reactor (SBR) system is typically used to benchmark the performance of hydrogen recombiner catalyst formulations. The catalyst performance in the SBR system is obtained as the rate of hydrogen recombination (in units of cm^3 of hydrogen per gram of catalyst per second).

3.1.1 SBR System Description

The SBR is a continuous flow stirred tank reactor (CSTR) that was specifically designed to test catalysts for their ability to safely remove hydrogen or its isotopes from gas streams. During normal operation of the SBR, reactor temperature, pressure, rotation speed of the reactor and total gas flow rate are kept constant, and the outlet hydrogen concentration is maintained steady by the varying the inlet concentration. The catalyst activity (reaction rate) is determined by the change in hydrogen concentration at the inlet and the total flow through the reactor.

The SBR system (see Figure 1) consists of a SBR reactor (with an inside diameter of 77.6 mm with a 425 cm^3 internal volume), catalyst basket or holder (stainless steel mesh with pockets varying from 3 to 13 mm in width), temperature controller, heating or cooling jacket, pressure gauge, a motor with a speed controller, a gas supply and gas analysis system. The inlet hydrogen concentration is set using mass flow controllers. After mixing, the hydrogen-in-air gas stream can be sent to the SBR either dry or humidified.

Figure 1. Photograph of the Spinning Basket Reactor (SBR) system.

3.1.2 Test Results and Analysis

The various formulations of catalyst were tested in the SBR system at dry and wet conditions in order to evaluate them in more than one scenario relevant to the potential atmospheric conditions of the application. The catalysts were tested in the SBR under the following conditions:

- Dry condition: outlet hydrogen concentration of 1500 ppm, dry gas, 20 °C, and a total flow of ~4 $L\cdot min^{-1}$.
- Immersed in deionized (DI) water for 1 h before testing: catalyst is immersed in DI water for 1 h prior to the test, then installed in the reactor and run under humid conditions, with an outlet hydrogen concentration of 2500 ppm, 100% RH, 30 °C, and a total flow of ~4 $L\cdot min^{-1}$.

The results from testing CatB, CatC, CatD and CatE compared with the benchmark catalyst (CatA), are provided in Figure 2. In general, the results demonstrate that compared with the benchmark catalyst, the catalysts supported on TiO_2 performed better under all conditions tested.

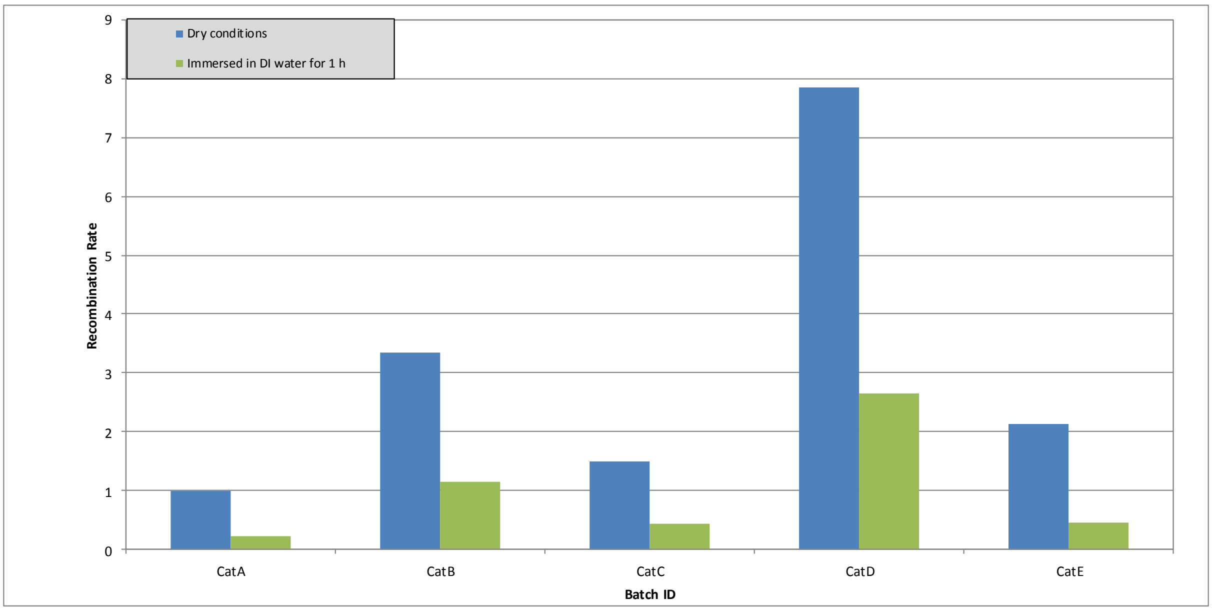

Figure 2. Summary of results from tests in the SBR.

Compared with CatB, CatC did not perform well in dry and immersed conditions, even though it was expected to perform better due to its higher wetproofed level. It was suspected that the higher wetproofing agent loading was causing the catalyst activity (recombination rate) measured in the SBR system to be reduced, since some of the additional wetproofing can block active sites of the catalyst. The recombination rate of CatD was significantly higher compared to the other TiO_2 supported catalysts. The increase in catalyst activity, possibly due to the higher surface area of the structure (6 mm rings), was greater than expected. Due to its high active metal concentration and low wetproofing concentration, CatE was expected to perform well in the SBR, particularly in the dry condition. However, as seen in Figure 2, CatE did not perform well compared with CatD. It is suspected that the difference in catalyst activity between CatD and CatE is due to the different catalyst support and/or catalyst preparation method.

4.0 APPLICATION SPECIFIC CATALYST TESTING

A thorough investigation is needed under conditions anticipated in radioactive waste storage in order to confirm a hydrogen recombiner catalyst will maintain its performance over the range of expected conditions and atmospheres. Several different catalyst test rigs at CNL with unique capabilities with respect to test conditions can be used to evaluate catalysts' performance.

A trickle bed recombiner (TBR) allows determination of the performance of catalysts under a flow of liquid water through the catalyst bed. This testing determines the adequacy of hydrophobic properties to provide the required performance from the catalyst. Evaluation of the performance under low oxygen conditions can be carried out in a Gas Phase Recombiner (GPR) system. Catalysts can also be tested in a system that allows potential catalyst contaminants to be injected into the reactor inlet gas stream. This test will be crucial for identifying a catalyst that can be applied to remove hydrogen in a waste storage container.

4.1 Trickle Bed Recombiner (TBR)

4.1.1 TBR Description

The Trickle Bed Recombiner (TBR) rig shown in Figure 3 is used is to evaluate the performance of recombiner catalysts. The TBR allows mixtures of hydrogen and oxygen (up to the stoichiometric ratio) to recombine in the presence of a catalyst in a vessel. Heat from the exothermic hydrogen-oxygen recombination reaction is removed by direct contact with recirculating water. The water passes through the catalyst bed, is cooled through a heat exchanger and then pumped back to the top of the recombiner vessel to trickle through the bed. The performance of the catalytic bed is evaluated by determining the concentration of unreacted hydrogen in the outlet stream from the reactor by gas chromatography. While operating pressure in this system is normally less than 35 kPag (5 psig), the design pressure of the vessels and the piping allow for possible deflagration occurring in the reactor vessel during recombination; however, all operational efforts are made to avoid this occurrence. The TBR consists of a reactor, gas supply system, recirculation water system, gas sampling system, gas analysis system, and a safety system. The TBR allows a variety of flow conditions so the effectiveness of the catalyst can be assessed. The maximum operating flows are 10 $L \cdot min^{-1}$ H_2 and 5 $L \cdot min^{-1}$ O_2.

Figure 3. Picture of the Trickle Bed Recombiner (TBR).

4.1.2 Test Details

CatA (baseline), CatB and CatC catalysts were tested in the TBR to determine how the catalysts supported on TiO_2 would perform compared with the SiO_2 supported catalyst under severe (i.e., wet) conditions. The tests were conducted with a hydrogen flowrate of 0.74 $L \cdot min^{-1}$ and an air flowrate of 2.06 $L \cdot min^{-1}$ in the TBR. The recycle water flowrate was maintained at 120 $mL \cdot min^{-1}$ and 20 – 25 °C during the tests.

4.1.3 Test Results and Analysis

The results from testing CatA, CatB and CatC catalysts in the TBR are provided in Figure 4. It should be noted that the vertical lines in some of the data in Figure 4 are from restarting the system after a shutdown. The results demonstrate that CatA is superior to the CatB and CatC catalysts under TBR conditions based on the stable hydrogen conversion over a period of about 19 days of operation. In contrast, the CatB and CatC catalysts did not last three days under the TBR conditions before the system interlocks were triggered due to high hydrogen concentration. The system automatically shuts down when the hydrogen concentration reaches about 2.2 vol.% in the outlet of the system.

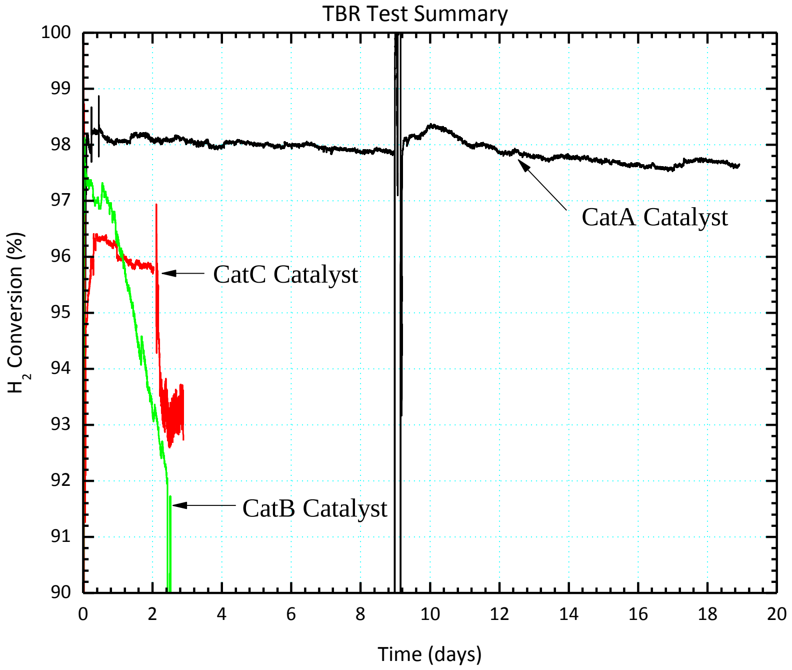

Figure 4. Summary of results from TBR tests on CatA, CatB and CatC catalysts.

It is considered that the continuous flow of water over the catalyst in the TBR makes it a more demanding test compared to the SBR system. Therefore, an increase in wetproofing agent concentration is expected to have a positive effect on the catalyst performance in the TBR system. The test results indicate (Figure 4) that the higher wetproofing agent concentration of CatC compared to CatB (see Table 1) did improve the performance of the catalyst under TBR conditions. The catalyst activity in the test with CatB catalyst steadily decreased and triggered the system to shut down after about 2.2 days. In comparison, the CatC catalyst steadily decreased at a much lower rate than CatB. After the TBR system was shut down and restarted, the performance of CatC dropped and did not recover after operation for several hours.

Ultimately, the performance of CatB and CatC catalysts in the TBR was much poorer than the CatA formulation. It is expected that the superior performance of the CatA formulation in the TBR is due to the catalyst support material. It was decided not to conduct further testing in the TBR with CatD or CatE because of the inferior performance of TiO_2 supported catalysts relative to the SiO_2 supported catalyst. Also, there is a known compatibility issue between 6 mm rings and the TBR process. The geometry of the rings is such that some of the cooling water is not allowed to reach the surface of the catalyst, which has been known to cause some local hydrogen combustion and destroy some of the catalyst in the TBR.

The results from the TBR tests provide insight into the characteristics of the CatB and CatC catalysts, but do not eliminate them from being candidate catalysts for use in the waste management application. The TBR test conditions are much more demanding on the catalyst with respect to water exposure than a waste storage tank. However, there are some instances in waste storage tanks, particularly for waste transfer, where the catalyst could be immersed in water (or the waste solution). It is now understood that the catalysts prepared with TiO_2 are not as hydrophobic as catalysts supported on SiO_2. The results from the TBR conflict with the SBR test results, which suggests that the TiO_2 supported catalysts are better than the CatA material in wet/water soaked conditions. However, the TBR test is considered more realistic since it is on a much larger scale, operates with higher hydrogen concentrations, and most importantly, operates for extended periods of time.

5.0 FUTURE WORK

Further tests, specific to the target application, are required to confirm that the selected catalysts are suitable for waste storage. Application specific tests are planned with the CNL hydrogen recombiner catalysts provided in Table 1 in experimental systems that have the capability to evaluate catalyst performance under a variety of conditions.

Tests are planned to be performed at low oxygen (air) concentrations in a gas phase recombiner (GPR) system, which is designed to test the performance of hydrogen recombiner catalysts over a range of flow rates and hydrogen concentrations. Low oxygen atmosphere is a potential condition for waste storage applications, where the oxygen produced through radiolysis is not in stoichiometric proportion to hydrogen as a result of the higher frequency of oxidation reactions in the waste tank atmosphere.

Tests will also be performed in the catalyst activity bench scale (CABS) system, which has the distinct ability to incorporate contaminants in the gas supplied to the reactor. After a review of the potential contaminants in waste storage headspace, ammonia (NH_3) and nitrous oxide (N_2O) were selected as contaminants for the CABS system. VOCs that are present in waste storage were also reviewed. A number of VOCs will be selected and tested in the CABS system. The compounds selected will be based on their abundance in the waste storage tank headspace, and their potential to poison the hydrogen recombiner catalyst.

6.0 SUMMARY

Waste storage was selected as the target application to pursue for CNL’s hydrogen recombiner catalysts. A number of hydrogen recombiner catalyst formulations have been selected and tested.

Through preliminary testing in the SBR, the catalysts supported on TiO_2 appeared to be more active than the baseline (CatA – Pt/SiO_2) recombiner catalyst. However, through lab-scale demonstration tests in the TBR, it was found that the CatA catalyst performs much better compared to CatB and CatC catalysts in severely wet conditions. The differences in the catalysts’ performance became evident in longer-term tests.

More laboratory-scale tests are planned to evaluate the performance (including catalyst lifetime) of CNL hydrogen recombiner catalysts in conditions more representative of a waste storage tank headspace. These tests will evaluate the catalysts’ performance in low oxygen environments and resistance to contaminants (VOCs, NH_3 and N_2O) typically found in waste tank headspace.

7.0 REFERENCES

1. J.L. Huckaby, L.A. Mahoney, J.G. Droppo, J.E. Meacham, “Overview of Hanford Site High-Level Waste Tank Gas and Vapor Dynamics”, Pacific Northwest National Laboratory Report, PNNL-14831, August 2004.

2. J.E. Meacham, “Steady-State Flammable Gas Release Rate Calculation and Lower Flammability Level Evaluation for Hanford Tank Waste”, Washington River Protection Solutions LLC, Richland, Washington, RPP-5926 R.8, November 2008.

3. Gardner, L., and Marcinkowska, K., AECL Passive Autocatalytic Recombiners, International Conference on Future of Heavy Water Reactors (HWR-Future), Ottawa, CNS, 2-5 October, 2011, Paper 41.

4. Seddon, W.A., Chuang, K.T., Holtslander, W.J., and Butler, J.P., AECL Wetproofed Catalysts: A New and Effective Solution for Hydrogen Isotope Separation and Hydrogen/Oxygen Recombination, Proc. ASME Energy Sources Technology Conference and Exhibition (84-PET-11), New Orleans, 1984.