HYDROGEN RECOMBINERS FOR NON-NUCLEAR HYDROGEN SAFETY APPLICATIONS

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ABSTRACT

Hydrogen recombiners are catalyst-based, hydrogen mitigation systems that have been successfully implemented in the nuclear industry, but have not yet received serious interest from the hydrogen industry. Recombiners have been installed in the containment buildings of many nuclear power plants to prevent the accumulation of hydrogen in potential accidents. The attractiveness of hydrogen recombiners for the nuclear industry is due to the confined state of the containment building, where hydrogen cannot be vented easily, and its passive design, where no power or actions are needed for the unit to operate. Alternatively, in the hydrogen industry, most applications utilize ventilation to mitigate potential hydrogen accumulation in confined areas and passive safety is not essential. However, many applications in the hydrogen industry may utilize hydrogen recombiners from a different approach. For instance, recombiners could be utilized in emerging hydrogen areas to minimize the costs of ventilation upgrades, or built into hydrogen appliances to avoid vent connections. The potential applications for recombiners in the hydrogen industry have different atmospheric conditions than the nuclear industry, which may impact the catalyst in the units and render them less effective. Thus, experiments have been performed to investigate the limits of the recombiner catalyst and if modifications to the catalyst can extend their use to the hydrogen industry. This paper will present and discuss the applications of interest, conditions that may affect the catalyst and results from experiments investigating the catalyst behaviour at temperatures less than 0 °C and carbon monoxide concentrations up to 1000 ppm.

1.0 INTRODUCTION

The hydrogen (H_2) economy is unfolding as a successor to the current hydrocarbon economy, mostly driven by the need to mitigate the negative environmental impact of carbon dioxide (CO_2) emissions resulting from the use of hydrocarbon fuels. The H_2 economy is underpinned by the widespread use of H_2 in the industrial sector and for transportation and energy storage. One of the main safety-related challenges associated with large-scale production, storage and use of H_2 is the potential for accumulation of flammable gas mixtures in confined or semi-confined areas, such as private garages, underground parking, and transportation tunnels. H_2 leak detection and mitigation measures are essential to ensure that it does not accumulate to combustible levels in the event of accidental releases. To prevent potential H_2 accumulation, the Canadian Hydrogen Installation Code mandates that all indoor H_2 installations be adequately vented to the outdoors with a minimum ventilation rate of 6 air changes per hour or 0.3 m^3/min per square meter of floor space, whichever is greater [1]. Similar requirements may be found in other jurisdictions. Notwithstanding this, there are scenarios where other H_2 mitigation measures may be complementary or preferable for operational reasons.

H_2 recombiners (also known as passive autocatalytic recombiners (PARs)) are a well-known technology for H_2 mitigation within the nuclear industry [2]. They may represent a complementary solution to ensure the safe indoor operation of systems utilizing H_2. In particular, deployment of H_2 recombiners has the potential to substantially reduce ventilation requirements while maintaining safe conditions, and ultimately provide a correspondingly significant reduction in capital and operating costs for H_2 installations. Recombiners operate by catalytically reacting (or recombining) H_2 and oxygen (O_2) to form water vapour and heat. The exothermic reaction on the catalyst drives a convective flow through the recombiner unit, allowing a self-starting, self-feeding and self-stopping process. H_2 recombiners start operation (known as self-start) at H_2 concentrations as low as

approximately 1 vol.%, making them capable of maintaining H_2 concentrations below the lower flammability limit (LFL) for H_2.

As the H_2 economy grows and H_2 technologies are applied within existing infrastructure, the likelihood of H_2 and hydrocarbon fuels being used in the same facility will be unavoidable. In addition, the ambient temperatures of the H_2 installations may be well below room temperature ($\sim20\,°C$). Thus, the immediate atmosphere around H_2 installations, such as vehicle maintenance facilities and parking garages may have low ambient temperatures ($< 0\,°C$) and in many instances, contains diesel engine exhaust, which consists of relatively high concentrations of known catalyst poisons like carbon monoxide (CO) and nitrogen oxides (NO_x). This paper will discuss the investigations on the low temperature limits of the recombiner catalyst, the susceptibility of the recombiner catalyst to CO poisoning and the development of a catalyst with increased resistance to CO poisoning.

2.0 BACKGROUND

2.1 Hydrogen Recombiner Description

The standard H_2 recombiner design consists of an open-ended rectangular box with an attached cover (Figure 1). An exothermic reaction occurs on the surface of the catalyst when H_2 and O_2 are present in the atmosphere, forming water vapour and heat.

$$H_2 + ½O_2 \rightarrow H_2O \qquad \Delta H = -241.81\,kJ/mol$$

The heat of reaction creates a natural convective flow through the recombiner. Warm humid air with unreacted H_2 are exhausted through the top grating. The principle of the H_2 recombiner operation is shown in Figure 1. The recombiner is passive, therefore does not require power or operator action to function. It self-starts in the presence of H_2-air mixtures. Owing to its compact design, the recombiner can be easily installed individually or in groups, and the modular design facilitates distribution of the required H_2 removal capacity throughout the building. The catalysts used in H_2 recombiners have a high activity for H_2 oxidation. Due to the CNL's proprietary wetproofed coating, they are not deactivated by water vapour or steam, and operate over a wide range of temperatures. Water is repelled, but H_2 and O_2 are able to diffuse to the active sites of the catalyst for the recombination reaction to occur.

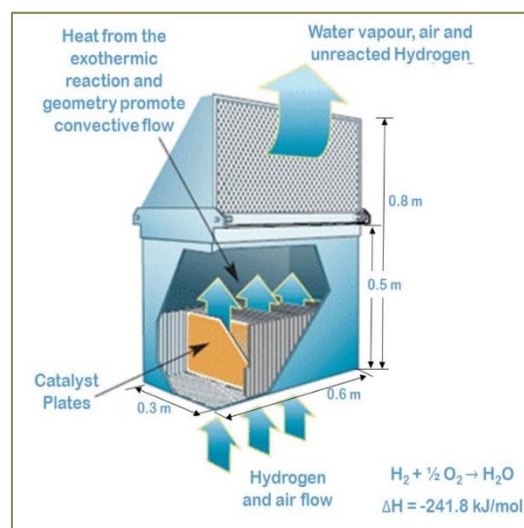

Figure 1. Principle of H_2 recombiner operation

2.2 Definitions

2.2.1 Self-Start Threshold

Self-start threshold is defined as the minimum H_2 concentration required to develop self-sustained convective flow through the recombiner at a given temperature. Self-start manifests itself as a sharp increase in the catalyst temperature. In a test, self-start is apparent when the temperature of the catalyst rises at least 50 °C above the initial (ambient) temperature for each volume percent H_2 in the atmosphere. Typically, at the same initial temperature, pressure and relative humidity, the catalyst plates are exposed to step increases of the H_2 concentration for 30 minute intervals until self-start occurs. The temperature increase is indicated by measuring the temperature at the centre of the catalyst plate (or coupon) using a thermocouple held in contact with the surface of the catalyst.

2.2.2 Recombination Rate (Capacity)

H_2 recombination rate (or capacity) is the amount of H_2 that a recombiner removes/recombines per unit of time (commonly expressed in kg/h). Capacity has been found to be a function of H_2 concentration, temperature, pressure and the geometry of the recombiner (size of the housing and/or amount of catalyst). For a given recombiner, capacity is experimentally determined from the rate of H_2 depletion in the test chamber, and, if necessary, corrected for leakage and gas removal from sampling.

The standard PAR recombination rate at 4 vol.% H_2, 25 °C and 100 kPa is 0.8 kg H_2/h.

2.3 Atmospheric Contaminants from Diesel Exhaust

As indicated above, some H_2 installation atmospheres may contain a certain level of CO and NOx from fossil fuel exhaust. It is expected that many H_2 installations will service H_2-electric, battery-electric and fossil fuel powered vehicles during the period leading up to 2050, when fossil fuelled vehicles are expected to no longer be available. Therefore, the atmosphere of H_2 installation may contain diesel engine exhaust, which has a relatively high concentration of CO and NOx (e.g., 100 to 500 ppm CO and 50 to 1000 ppm NOx) [3]. Adsorption of CO molecules on platinum (Pt) metal catalyst can hinder the catalyst reaction by blocking the active sites, resulting in temporary, reversible degradation of the catalyst [4]. The CO level examined in the earlier studies on the AECL/CNL H_2 recombiner was greater than 1000 ppm [4], which is significantly higher than what is expected in the maintenance garage (< 1000 ppm). More studies are required to quantify the impact of lower CO levels (~100 ppm) on the self-start thresholds of the existing AECL/CNL H_2 recombiner technology. Depending on the results, development of suitable catalyst that can oxidize H_2 in the presence of CO may be needed. NOx may have a similar effect on the existing recombiner catalyst; however, relevant studies have yet to be performed.

2.4 Previous Hydrogen Recombiner and CO Experiments by CNL

H_2 recombination in the presence of CO has been studied by CNL, since severe accidents in nuclear reactors have the potential to release both H_2 and CO. Studies to date have dealt with high concentrations of CO (0.2 – 8 vol.%) [4]. It should also be noted that in nuclear accident scenarios H_2 is typically released in the early phase of an accident, so the catalyst and surrounding gas may have heated up due to the recombination of H_2 before the H_2 and CO are generated in the late phase of the accident. The previous studies have found that when the recombiner catalyst temperature is greater than 70 °C, the CO will react on the catalyst surface to form CO_2, in parallel to the H_2 recombination. However, when the catalyst is less than 70 °C, CO concentrations as low as 0.2 vol.% were found to poison the catalyst. The CO poisoning effect is reversible and the recombiner can restore its activity when it is re-exposed to a CO-free H_2–air mixture [4].

3.0 EXPERIMENTAL

3.1 Materials

Five different formulations of recombiner catalyst were investigated for CO tolerance. Four of the five catalysts were developed by combining Pt and iridium (Ir) as the active metals and using different catalyst preparation techniques. The standard AECL/CNL H_2 recombiner catalyst formulation, known as Type 99-11, was used as a benchmark for the new formulations of catalyst. The new catalysts are identified as CO-CAT01 through CO-CAT04. All of the four new catalyst formulations have the same Pt loading as the benchmark Type 99-11, but have varying Ir loadings. The relative Ir loadings of the four new catalyst formulations are CO-CAT01 = CO-CAT02 < CO-CAT03 < CO-CAT04. CO-CAT01 and CO-CAT02 were made using different catalyst preparation methods.

3.2 Test Facilities for Hydrogen Recombination and Carbon Monoxide Tolerance

3.2.1 Hydrogen Safety Test Facility (HSTF)

The HSTF is a structural steel spherical pressure vessel (shown in Figure 2) with an internal free volume of 0.25 m^3 and a pressure rating of up to 1.72 MPa. The facility has systems for the addition of H_2, CO, steam and air. Further details on the HSTF are provided by Gardner et al. [5]. The facility has multiple Xensor 5320 point-type thermal conductivity detector (TCD) sensors, a Xensor 5320 high pressure TCD sensor for in-line gas analysis, and a GOW-MAC gas chromatograph (GC) equipped with a TCD to measure multiple gas concentrations within the vessel (including H_2 and CO). A hazardous atmosphere qualified muffin fan is used to ensure well mixed conditions within the sphere during gas addition. It should be noted that the GC was not used in this series of experiments since the CO concentrations tested were below the detection limits of the instrument. The H_2 and CO concentrations were determined by the Xensor point-type sensors and by partial pressure measurements, respectively. The maximum uncertainty of the CO concentrations was within ±15% (relative) and the H_2 concentrations was within ±0.2 vol.% (absolute).

A scaled version of the H_2 recombiner was developed for the HSTF, based on the recombiner geometry used in the Containment Test Facility (CTF) at Whiteshell Laboratories (WL). As shown in Figure 2, it is an open-ended rectangular box with no cover, with the intent for three catalyst coupons to be installed in it. Details on the scaling between the facility and recombiner are provided by Gardner et al. [5]. For the experiments to investigate the self-start of the recombiner in the presence of low concentrations of CO, three 4 by 6 cm catalyst coupons were installed in the scaled-recombiner housing.

Analog to digital data-acquisition hardware was used for recording the thermocouple and pressure signals on a computer. LabVIEW software was used to interface with the data acquisition hardware. The signals were taken and recorded at 1 Hz. The Xensor sensor measurements were connected to and communicated with a personal computer via a CAN bus. The data was acquired using a LabVIEW program developed by Xensor Integration at a sampling rate of 1 Hz.
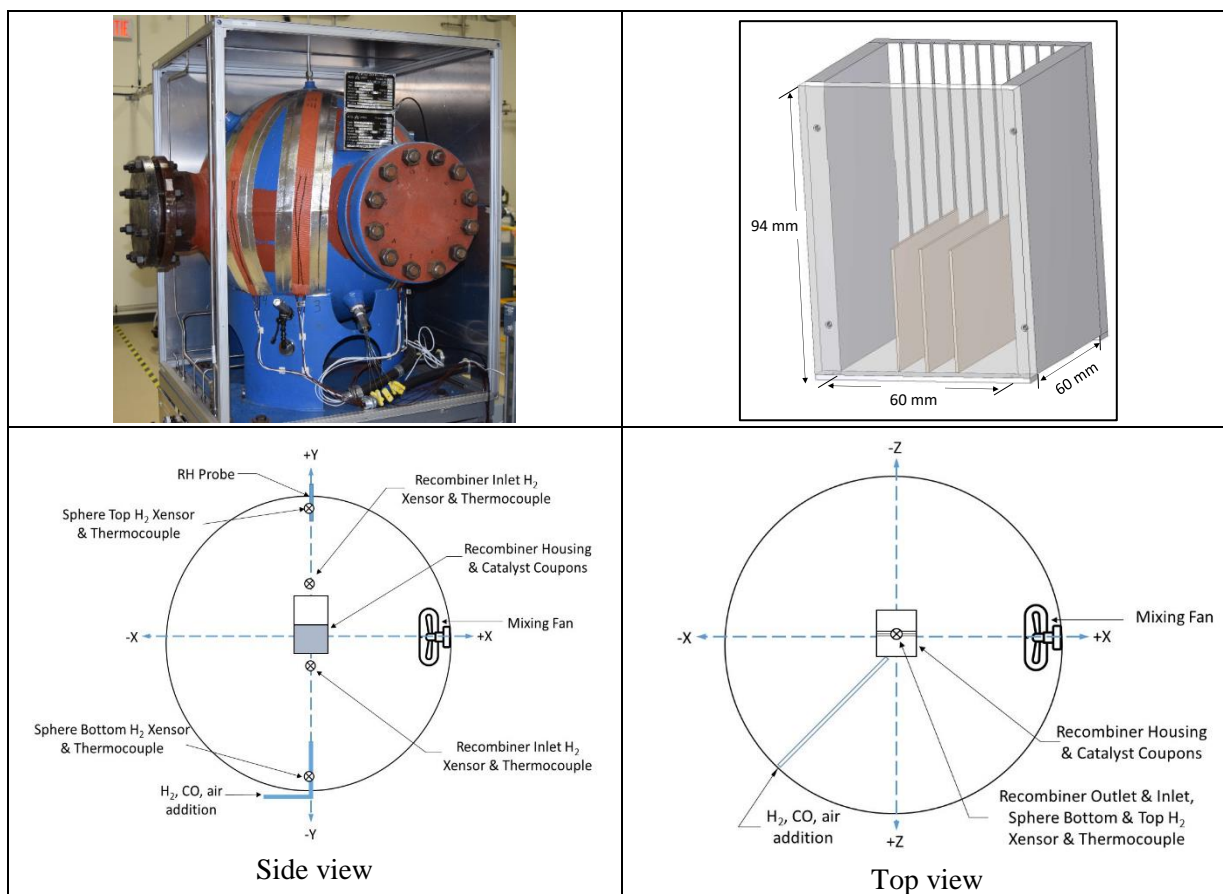
Figure 2. HSTF photograph (top left), schematics with recombiner and instrumentation (bottom left and right), and a three dimensional rendering of the reduced-scale recombiner developed for the HSTF

3.2.2 Catalyst Activity Bench-Scale (CABS) System

The catalyst activity bench-scale (CABS) test rig was designed and constructed to conduct bench-scale testing on H_2 recombiner catalysts with potential poisons aiming to observe their effects on catalyst activity. The main components of the CABS rig include gas supply, the glass reactor vessel (6-L volume, 14.6-cm inner diameter - ID) with a heating jacket, humidifier vessel, gas analysis equipment, and a data acquisition system (see Figure 3).

A gas cylinder with 1000 ppm CO and a balance of air was connected to the CABS test rig to investigate the CO tolerance on the new catalyst formulations. H_2, air and CO flow rates were regulated by mass flow controllers (MFCs) to yield the desired gas mixture composition.

The heating/cooling jacket of the vessel was filled with ethylene glycol (boiling point 197 ºC at 101.3 kPa) that was continuously circulated using a temperature controlled bath circulator, which enabled test temperatures as low as -10 ºC and up to 20 ºC.

Catalyst coupons (2 cm wide x 10 cm long) were suspended near the centre of the glass vessel from an alligator clip. The gas temperature in the reactor and the catalyst temperature were monitored with Type K thermocouples, and a pressure gauge was used to monitor the vessel pressure.

Temperatures were recorded at the top of the reactor (vessel outlet), bottom of reactor (vessel inlet) and in the centre of the catalyst sample. H_2 concentrations were measured using two Xensor 5320 point-type TCD sensors installed in the top and bottom of the CABS vessel. In addition, H_2 and CO concentrations were measured with an Agilent Technologies Model 6890N GC equipped with a TCD and an automated gas-sampling valve maintained at constant temperature. The GC was calibrated

using a certified H_2-in-nitrogen gas standards. The data acquisition for the CABS test rig is identical to HSTF (see Section 3.2.1).
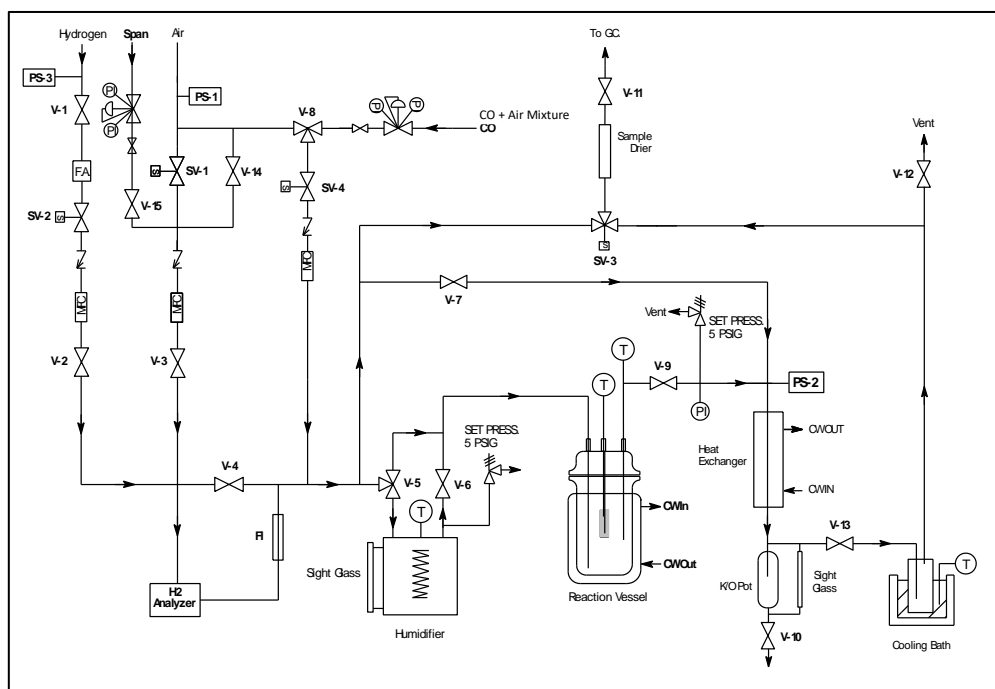

Figure 3. Schematic of the CABS test system

3.3 Test Procedure

3.3.1 Hydrogen Safety Test Facility (HSTF)

The basic process for carrying out the tests to determine the H_2 recombiner catalyst self-start behaviour with low concentrations of CO in the HSTF begins with sealing the test vessel and performing a leak check. The vessel was then filled with air at an initial pressure of 100 kPa and the Xensor sensors were zeroed to ensure a good baseline for H_2 measurements in the vessel. To give 1 vol.% (10,000 ppm) CO in the mixture, 1 kPa of CO was added to the vessel. Then air was added up to a total pressure of 500 kPa to dilute the CO concentration in the vessel by five times. The vent was opened to reduce the vessel pressure to 100 kPa (no change in the CO concentration). Air was then added to the required pressure to dilute and achieve the desired level of CO concentration. The vent valve could then be opened to reduce the vessel pressure to 100 kPa. In order to let the vessel pressure equalize and the conditions to settle in the vessel, a five minute waiting period was given after the vent valve was closed. The mixing fan was then turned on and H_2 was added until the Xensor sensors read 0.5 vol.% H_2. Once the H_2 addition was completed, the mixing fan was turned off, and a maximum duration of 30 minutes was given to allow the catalyst to begin to react. If no significant catalyst temperature was observed, the H_2 concentration was increased by 0.5 vol.% and the 30 minute waiting was repeated until a maximum of 3 vol.% H_2 in the vessel was reached. When the catalyst temperature increased significantly (e.g., greater than 50 °C), self-start was noted and the purge cycle was performed. This sequence was performed for CO concentrations at 100, 300, 500, 700, 900 and 1000 ppm.

3.3.2 Catalyst Activity Bench-Scale (CABS) Test System

The tests in the CABS test rig investigated the self-start behaviour and H_2 conversion of the recombiner catalyst with low concentrations of CO. In addition, a separate series of tests were performed to investigate the self-start performance of the standard recombiner catalyst at temperatures as low as -10 °C. The basic steps followed to perform the test are discussed below.

The water bath was turned on to heat or cool the vessel to the desired temperature. Once the vessel jacket and gas inside the vessel reached the desired temperatures, the air flow rate on the MFC was set to 2.9 L/min, then the air valve was opened. Once a steady flow of air was established, the desired flow rate of H_2 to provide 3 vol.% of H_2-in-air to the CABS reactor was set to establish a baseline. Then, sampling the reactor inlet gas concentration with the GC was initiated and run until the measurements were stable. The reactor outlet stream was then measured with the GC until the measurements were stable. The H_2 valve was closed to stop the H_2 flow and the air flow rate was increased to 3 L/min. In order to start the tests with CO without residual heat from the baseline test in the system, the next step is not started until the catalyst temperature has decayed to ambient temperature. Once the catalyst temperature is stable at approximately 20 °C, the air flow was adjusted and the CO-air mixture flowrate was set to deliver the desired CO concentration to the system. Then, the valve (V-8) to introduce CO to the CABS reactor was opened. To allow any poisoning process to take place on the catalyst surface, 0.5 vol.% H_2 was introduced to the gas mixture after a five minute waiting period. If no significant catalyst temperature increase was observed 30 minutes after the H_2 was introduced, the H_2 concentration was increased by 0.5 vol.% and the 30 minute waiting was repeated until a maximum of 3 vol.% H_2 in the vessel was reached. If the catalyst temperature increased significantly (e.g., greater than 50 °C), the H_2 concentration was increased to 3 vol.% and the inlet and outlet streams were measured with the GC. Once the test sequence was completed, the system was purged with air, all the valves were closed and, the water bath was turned off.

For tests to investigate the low temperature limits (from -10 to 20 °C) on the self-start performance of the standard AECL/CNL catalyst, the same sequence of testing was performed; however, after the baseline test was performed at 20 °C, the water bath temperature was reduced with the vessel sealed. The self-start testing sequence was performed in the same manner, but without the addition of CO-air gas mixture.

4.0 RESULTS AND DISCUSSION

The results obtained from various experiments are presented and discussed in this section. They include results to evaluate the new Pt-Ir catalysts for recombination activity in the presence of CO and to determine the recombination performance of the standard AECL/CNL recombiner catalyst at low temperatures.

4.1 Hydrogen Recombination and Carbon Monoxide Tolerance

4.1.1 Results from the HSTF

The HSTF was used to explore the CO-tolerance of the recombiner catalysts in a geometry that approximates a confined or semi-confined H_2 installation application. The results from the experiments to investigate the minimum H_2 concentration to generate a self-start at a given CO concentration are provided in Figure 4. H_2 was added in stepped increments of 0.5 vol.% to the vessel, thus the accuracy of the self-start H_2 concentration at a given CO concentration is limited to the step size of 0.5 vol.%.
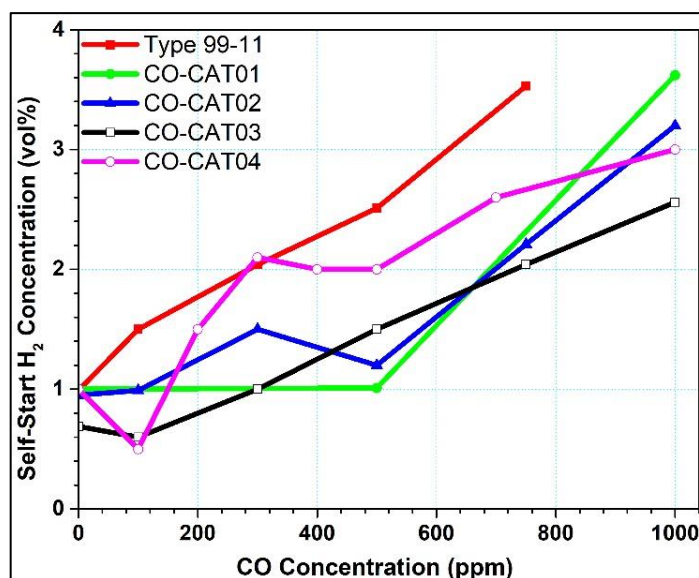
Figure 4. Results from H_2 self-start tests with CO and new Pt-Ir H_2 recombiner catalysts in the HSTF

In general, the newly developed Pt-Ir catalysts have a similar response to H_2 as the reference recombiner catalyst (Type 99-11), but show a significant improvement in CO resistance. There is a noticeable trend that all of the recombiner catalyst formulations tested follow that as the CO concentration increases, the self-start H_2 concentration also increases. This trend suggests that the low concentrations of CO reduce the activity of the catalyst for the H_2 recombination reaction.

As reported by Grenier [3], up to 500 ppm of CO may be present in maintenance garages. If this is taken to be the target maximum CO concentration, the results from the tests in the HSTF suggest that the standard H_2 recombiner catalyst, Type 99-11, would require approximately 2.5 vol.% H_2 to self-start. While 2.5 vol.% is below the LFL of H_2, there is little margin between the potential self-start concentration of Type 99-11 and the LFL. A small margin may not be acceptable when considering high H_2 release rates where the H_2 concentration can increase quickly by accumulating in a confined area or stratifying.

The Pt-Ir catalyst formulations reduce the H_2 concentration required for self-start to about 1 vol.% at 500 ppm CO. However, some performance differences exist among the new catalyst formulations. At CO concentrations up to 500 ppm, the catalyst formulation that performed the best was CO-CAT01. However, at the higher CO concentrations, CO-CAT01 had the worst performance among the new formulations tested requiring 3.6 vol.% H_2. CO-CAT04 was outperformed by the other new formulations, quite consistently, at the different CO concentration levels. CO-CAT02 and CO-CAT03 were considered to perform the best over the full range of CO concentrations tested. It should be noted that both CO-CAT02 and CO-CAT03 were also tested with 1500 ppm CO. However, no self-start was observed in both instances with a maximum of 3.5 – 4.0 vol.% of H_2 added to the vessel.

Since the Pt concentration of all the H_2 recombiner catalyst formulations was the same, but the Ir loading varied, some observations can be drawn from the Ir differences and the results in the HSTF. It is evident that there is an optimal Ir loading that serves the self-start performance best. CO-CAT04 with the highest Ir loading did not perform as well as the catalysts loaded with the lower and intermediate Ir loadings. In addition, CO-CAT02, CO-CAT03 and CO-CAT04 were prepared by the same method compared to CO-CAT01, so the method to prepare CO-CAT01 can be considered to be inferior.

A sample of one of the new catalyst formulations was evaluated for H_2 recombination rate to verify that the modification to the catalyst did not impact the recombination rate performance. The test was performed with H_2/air mixtures only. A comparison between the experimentally determined H_2

recombination rate (scaled with a value of 180 discussed in Reference [5]) and the H_2 recombination rate equation (not shown here but discussed in [6]), which represents an average of the full-scale recombiner data, is shown in Figure 5. The experimental data compares well with the recombination rate equation, which suggests that the H_2 recombination rate performance is not affected by the addition of Ir to the catalyst. This result is not surprising as the H_2 recombination rate is limited by mass transfer to the catalyst surface which is influenced by the fluid dynamic properties, compared to the self-start which is limited by surface reaction kinetics [7]. Based on this understanding of the mechanism behind the H_2 recombination rate, the H_2 recombination rate of all the Pt-Ir catalyst formulations are not impacted by the catalyst modifications. It should be noted that above 5 vol.% H_2 the experimental data begins to deviate from the recombination rate equation. As detailed by Gardner et al. [5], this deviation is an artifact from the large-scale testing.
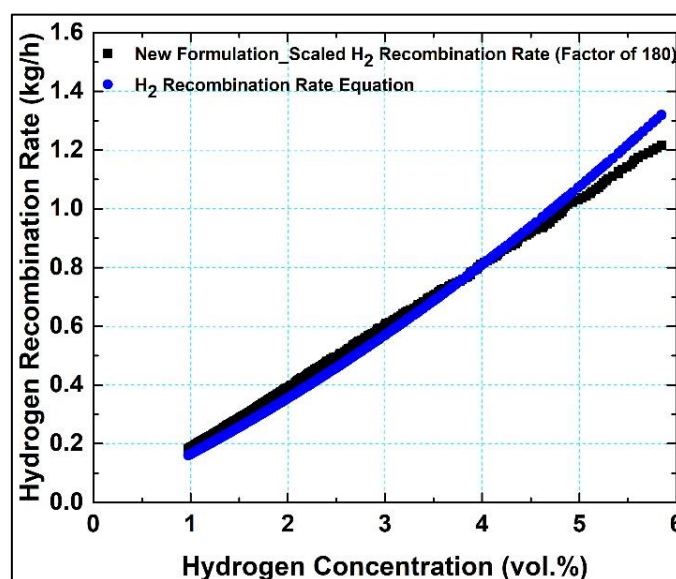

Figure 5. Comparison of new catalyst formulation experimentally determined recombination rate and the AECL H_2 recombination rate equation

4.1.2 Catalyst Activity Bench-Scale (CABS) Test Rig

Tests to determine the limit of CO tolerance of the original H_2 recombiner catalyst formulation (Type 99-11) and new H_2 recombiner catalyst formulations were performed in the CABS test rig at approximately 20 ºC, atmospheric pressure and dry conditions. Compared with the HSTF, the data from the CABS rig cannot easily be scaled to relate to a full size H_2 recombiner; however, with finer control of gas concentrations and lower gas analyzer detection limits, a more accurate relative comparison between catalyst formulations can be made. Similar to the HSTF, H_2 was added in stepped increments of 0.5 vol.% to the CABS vessel, thus the accuracy of the self-start H_2 concentration at a given CO concentration is limited to the step size of 0.5 vol.%. The data obtained from the tests included (1) the minimum H_2 concentration required for the catalyst to self-start at given CO concentrations, and (2) the H_2 conversion at given CO concentrations

A summary of the results from the self-start H_2 concentration tests is provided in Figure 6. A summary of the H_2 conversion values from the CABS tests is provided in Table 1. It should be noted that since the conversion results are provided at given H_2 and CO concentrations, not all the values for each catalyst formulation are provided in Table 1. To assess the conversion or steady-state catalyst temperature values at the same condition, the most common self-start H_2 concentration at a given CO concentration was selected. For instance, at 100 ppm a majority of the catalyst formulations self-started at 1.0 vol.% H_2 (as shown in Figure 6). Thus, the catalysts that self-started at 1.0 vol.% H_2 are represented in Table 1 (i.e., CO-CAT01, CO-CAT03, and CO-CAT04).

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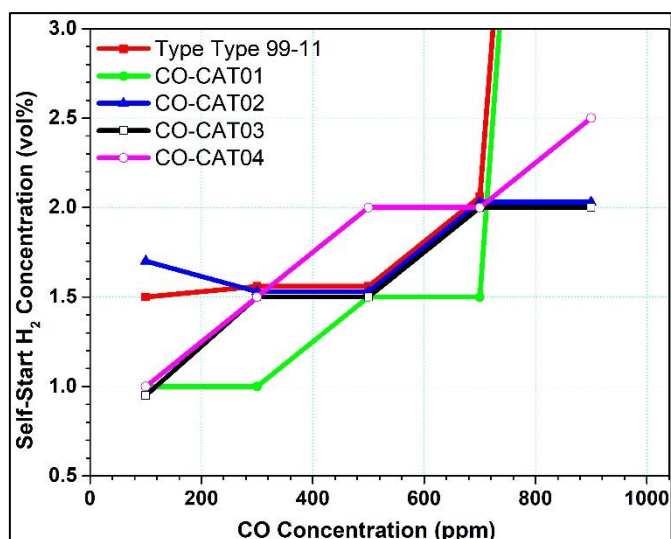Figure 6. Results from H₂ self-start tests with CO and new recombiner catalysts in the CABS test rig

The results from the CABS tests regarding the self-start H_2 concentration (see Figure 6), suggest that CO-CAT01 has the lowest self-start H_2 concentration values compared with all other formulations. However, CO-CAT01 failed to self-start at 900 ppm CO with up to 3.0 vol.% H_2. This result is consistent with the HSTF test on CO-CAT01 (see Figure 4), where greater than 3 vol.% H_2 was required for the catalyst to self-start with 1000 ppm CO. CO-CAT04 was found to have a higher self-start H_2 concentration at each CO concentration compared with the other catalyst formulations, with exception to 100 ppm CO. Though, it did self-start at 900 ppm CO. The results from CO-CAT04 in the CABS test rig are consistent with the HSTF results.

The self-start H_2 concentration for Type 99-11 catalyst was similar to the new Pt-Ir catalyst formulations that performed well in the CABS, but failed to self-start at 900 ppm CO with 3 vol.% H_2. Similar to the HSTF tests, CO-CAT02 and CO-CAT03 had the best overall self-start H_2 concentrations of the catalysts tested. Between the CO-CAT02 and CO-CAT03 formulations, the later consistently performed better than the former.

The H_2 conversion values (conversion = 100% * ([H₂]$_{inlet}$ − [H₂]$_{outlet}$)/[H₂]$_{inlet}$) presented in Table 1, can provide some insight into the steady-state performance of the catalyst during the experiments in the CABS test rig. Regardless of the presence of CO, the H_2 conversion results suggest that at 2 vol.% H_2, the catalyst has reached its peak performance. This is found from comparing the baseline (3 vol.% H_2) results and the test results with 2.0 vol.% H_2. Another observation made from this data is that the Type 99-11 catalyst does not seem to perform as well as the Pt-Ir catalysts at the different CO concentration steps. The H_2 conversion values are consistently lower than the conversion of the Pt-Ir catalysts.

Table 1. Summary of H₂ conversion with CO in CABS test rig experiments

Catalyst Formulation	H₂ Conversion (%)					
	Baseline at 3 vol.% H₂	100 ppm CO, 1.0 vol.% H₂	300 ppm CO, 1.5 vol.% H₂	500 ppm CO, 1.5 vol.% H₂	700 ppm CO, 2.0 vol.% H₂	900 ppm CO, 2.0 vol.% H₂
Type 99-11	55.6	-	35.0	34.0	47.8	No self-start
CO-CAT01	59.9	33.0	-	51.6	-	No self-start
CO-CAT02	58.2	-	53.6	52.3	55.8	55.5
CO-CAT03	59.0	30.7	38.1	48.7	52.5	55.2
CO-CAT04	57.0	33.3	51.0	-	53.9	-

4.2 Low Temperature Tests

A series of experiments were performed in the CABS test rig at temperatures below room temperature to understand the self-start performance of H_2 recombiner catalysts operating in H_2 installations without heating in colder climates. Since the reaction rate and activation energy are dependent on temperature, historically there has been scepticism of the ability of the recombiner catalyst to function at low initial ambient temperatures.

The tests in the CABS test rig were performed at near atmospheric pressure and in dry conditions from -10 to 20 °C. The gas in the vessel was cooled until the desired temperature was reached, then a H_2-air mixture was introduced to the CABS vessel with a total flow rate of 3 L/min. The gas supplied to the system was pre-cooled to ensure the gases did not add additional heat to the vessel. Only the standard AECL/CNL H_2 recombiner catalyst (Type 99-11) was tested. The results from the series of tests are provided in Figure 7. As can be seen in the figure, at temperatures as low as -10 °C, the standard AECL/CNL recombiner catalyst will self-start at H_2 concentrations below the LFL. However, there is a clear trend indicating that as the initial ambient temperatures decrease, the H_2 concentration required for self-start increases. In Figure 7, the black symbols indicate the test conditions attempted where a self-start was achieved. Conversely, the red symbols indicate the test conditions attempted where no self-start was observed. It is evident in the graph that at the lower temperatures the accuracy of the test was improved, where the red and black symbols are closer together, compared with the tests at higher temperatures. For instance, at 10 °C, the test found that no self-start occurred at 1.0 vol% H_2, but self-start did occur at 2.4 vol% H_2. This test was not repeated with lower H_2 concentration since the data at 5 °C indicated a self-start a lower H_2 concentration. It is expected that at 10 °C, the self-start H_2 concentration is approximately 1.5 vol%. The difference in the self-start and no self-start results identify the boundary where the catalyst will function and where it will not. The trend found in Figure 7 can be used to extrapolate to colder temperatures to identify the limit of the recombiner self-start H_2 concentration.
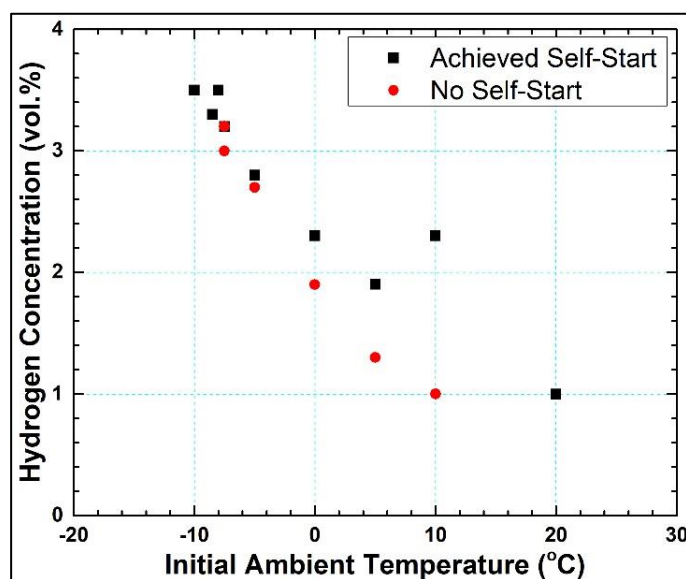

Figure 7. Results from H_2 self-start tests with the standard AECL/CNL H_2 recombiner catalyst (Type 99-11) at low temperatures in the CABS test rig

5.0 CONCLUSION

The standard PAR catalyst, Type 99-11, and a number of new catalyst formulations containing Ir were developed, characterized and tested to determine their tolerance for CO at low concentrations. The following conclusions were found from the catalyst development and testing.

The addition of Ir to the H_2 recombiner catalyst successfully increases the catalyst H_2 recombination activity in the presence of low concentrations of CO (< 1000 ppm). However, selected catalyst formulations demonstrated better CO tolerance than others. CO-CAT02 and CO-CAT03 catalyst formulations were notable, self-starting at H_2 concentrations as low as 1 vol.% with 500 ppm CO while 1.5 vol.% H_2 was required for Type 99-11. The results from the tests performed in the HSTF and CABS test rig were consistent. The general trend as well as the specific trends of the catalyst formulations were congruent between the two test systems. Finally, the addition of Ir to the recombiner catalyst did not affect the recombination rate. The next steps to investigate the CNL's H_2 recombiner for H_2 installations include understanding the effect of NO_x on the recombiner performance and assessing the economics of H_2 recombiners versus mechanical ventilation.

The results from the tests at low initial ambient temperatures (in Figure 7) suggest that at temperatures as low as -10 °C, the standard AECL/CNL recombiner catalyst will self-start at H_2 concentrations below the LFL. A clear trend was found indicating that as the initial ambient temperatures decrease, the H_2 concentration required for self-start increases.

6.0 REFERENCES

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