# Manufacture, Assessment and Down-Selection of Catalysts for the Decomposition of Hydrogen Peroxide

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## Abstract

Two sets of experimental apparatus have been developed to assess the performance of catalysts intended to decompose 87.5% hydrogen peroxide. Both procured and manufactured heterogeneous catalysts have been tested. These have different chemical and geometrical characteristics and consist of wire gauzes, metal foams and coated or impregnated ceramic pellets. The first apparatus, the sealed reactor, was designed to assess the catalyst start-up characteristics. The second apparatus provides data on the structural integrity and longevity of the catalyst using a mass-loss technique. As a result three catalysts have been identified as having promising characteristics and require further investigation.

## 1. Introduction

The space community relies heavily upon hydrazine-based fuels for use within secondary propulsion systems on board satellites and spacecraft. However, increasingly stringent controls on human exposure to these highly toxic propellants have led to a rise in the associated cost of propellant handling, storage and transportation. It is due to these increasing costs, in combination with damaging environmental effects, that there is a renewed interest in 'green' or low toxicity propellants [1,2]. Hydrogen peroxide at high concentrations (>80%) is regarded as one such propellant. Upon decomposition high temperature steam and oxygen are released, which can form the basis of either monopropellant or bipropellant thrusters. To achieve the required performance the decomposition of hydrogen peroxide must be catalysed.

One of the key challenges in the successful implementation of hydrogen peroxide based thrusters is the development of catalysts that are effective and have a long lifetime. Historically, silver in the form of wire gauze has been the mainstay of hydrogen peroxide catalysts [3]. However, silver's low melting point limits the concentration of hydrogen peroxide that can be successfully decomposed [4]. This, in combination with its poor low temperature performance, has resulted in the development of advanced catalysts which do not suffer these limitations. Nonetheless, due to its heritage, silver remains a baseline against which current catalysts are compared. The development of modern catalysts has mainly focused on ceramic substrates [5], which have been shown to significantly outperform silver gauze [6].

This paper describes the ongoing work to assess and as a result down-select a range of viable heterogeneous catalysts. The assessment considers the physical characteristics, effectiveness and lifetime of candidate catalysts using a range of experimental apparatus. This work is one aspect of a wide-ranging study into low toxicity propellants referred to as the GRASP (GReen Advanced Space Propulsion) project [7], which is funded by the EC under the FP7 Program.

## 2. Catalyst Procurement and Manufacture

The current paper reports on the findings of 18 ceramic based-catalysts, 3 metallic foam-based catalysts and 12 metallic gauze catalysts. Both procured and manufactured catalysts have been assessed, with all catalyst manufacturing being undertaken by the University of Southampton. Table 1 provides information on the procured catalysts; these have been tested as supplied and have consistent dimensions.

**Table 1: Summary of procured catalysts**

| Product Description | Form |
|---|---|
| Palladium on alumina, 0.5 wt. % loading | 3.2mm pellets |
| Ruthenium on alumina, 0.5 wt. % loading | 3.2mm pellets |
| Ruthenium on alumina, 2 wt. % loading | 3.2mm pellets |
| Platinum on alumina, 0.5 wt. % loading | 3.2mm pellets |
| Platinum on alumina, 1 wt. % loading | 3.2mm pellets |
| Platinum on alumina, 5 wt. % loading | 3.2mm pellets |
| Silver | 20 Mesh, gauze |
| Platinum | 45 Mesh, gauze |
| Palladium: Nickel (95:5 wt. %) | 50 Mesh, gauze |
| Platinum: Iridium (90:10 wt. %) | 150 Mesh, gauze |
| Platinum: Rhodium (90:10 wt. %) | 80 Mesh, gauze |
| Platinum: Rhodium: Palladium (90:5:5 wt. %) | 80 Mesh, gauze |

The metallic gauzes have also been subjected to a heat treatment process. During this process the gauzes were heated to 500 degrees C for several hours before being allowed to cool slowly.

Several metallic foam and ceramic pellet-based catalysts have also been manufactured. These catalysts are summarised in Table 2. Three manufacturing methods were employed, all based around a soaking and baking method. In all cases the base materials were first calcined at 500°C for two hours to drive off moisture and volatiles. The materials were then impregnated with a precursor solution of sodium permanganate monohydrate ($NaMnO_4 \cdot H_2O$) and distilled water. Finally they were dried and baked in a furnace resulting in the formation of an active phase consisting of oxides of manganese ($MnO_x$). The only difference between method 1 and 2 is a doubling of the soak time in method 2. This resulted in an increase in the catalyst loading on the ceramic substrate using the same catalyst support (Batch 004-006 vs. Batch 001-003). The difference between method 1 and method 3 was both a doubling in soak time and a significant increase in the baking temperature, approaching that of the melting point of the nickel base material.

**Table 2: Summary of manufactured catalysts**

| Form | Designation | Base Material | Diameter (mm) | Active Phase | Manufacture Method | %wt loading |
|---|---|---|---|---|---|---|
| Pellet | Batch 001 | $\gamma - Al_2O_3$ | 3.06 | $MnO_x$ | 01 | 13.0 % |
| Pellet | Batch 002 | $\gamma - Al_2O_3$ | 3.39 | $MnO_x$ | 01 | 24.5 % |
| Pellet | Batch 003 | Zirconia | 3.37 | $MnO_x$ | 01 | 11.2 % |
| Pellet | Batch 004 | Titanium Dioxide | 1.6 | $MnO_x$ | 02 | 16.5 % |
| Pellet | Batch 005 | Ceria* | 1.6 | $MnO_x$ | 02 | 19.1% |
| Pellet | Batch 006 | Quadri lobbed $\gamma - Al_2O_3$* | 1.0 | $MnO_x$ | 02 | 52.3 % |
| Pellet | Batch 007 | $\gamma - Al_2O_3$ | 3.06 | $MnO_x$ | 02 | 17.3 % |
| Pellet | Batch 008 | $\gamma - Al_2O_3$ | 3.39 | $MnO_x$ | 02 | 83.7 % |
| Pellet | Batch 009 | Zirconia | 3.37 | $MnO_x$ | 02 | 20.3 % |
| Foam | Batch 100 | - | - | Silver | ** | - |
| Foam | Batch 101 | Nickel Foam | - | $MnO_x$ | 02 | 97.3 % |
| Foam | Batch 102 | Nickel Foam | - | $MnO_x$ | 03 | 73.4 % |

* Catalyst supports provided by Céramiques Techniques et Industrielles (CTI) in France

** This foam was made using a method developed by the University of Southampton Chemistry Department

## 3. Sealed Reactor Testing

This initial assessment apparatus used to assess catalyst start-up characteristics. The sealed reactor is capable of providing a comparative ranking of similar types of catalysts. The apparatus comprises a constant-volume, sealed reactor, a detailed description of which can be found in [8]. In essence, a sealed chamber, or reactor, is connected to a small delivery tank containing 3 ml of 87.5% concentration hydrogen peroxide. The delivery tank is pressurised with nitrogen to a pressure of 10 bar absolute for pellets and foams, and 1.5 bar absolute for gauzes. The nitrogen pressure regulator is then closed to stop the nitrogen being replenished. The hydrogen peroxide is released by means of a solenoid valve, which then allows the liquid to settle at the base of a small decomposition vessel containing a fixed volume of catalyst. In all cases the valve is left open for the full length of the experiment. The oxygen and steam produced by the decomposition of hydrogen peroxide then flows upwards and through two stainless steel tubes, which exhaust into the main reactor chamber. The temperature at the exit of the decomposition vessel (and hence the entrance to the reactor chamber) and the pressure in the main chamber are recorded for later analysis using LabVIEW.

It should be noted that the sealed reactor is not designed to capture the true thermodynamic decomposition temperature. The reactor is not insulated in any way and its thermal capacity is very large. Nevertheless it allows the comparison of catalysts based on their initial performance.

### 3.1 Sealed Reactor Results

For experiments with ceramic-based and metallic foam-based catalysts the delivery valve open time was set to 60s, with full decomposition of the HTP normally being achieved within this time. However, the rate of decomposition was slower with the 12 metallic gauzes so, in these cases, the run time was extended to 180s.

Two initial datum runs were performed at the two delivery pressures investigated. These were both done with 1% platinum pellets in the reactor but no peroxide. The reactor pressures recorded in these datum runs were subtracted from the reactor pressure recorded from a “live” run with peroxide. This difference in pressure, or relative pressure, is a more sensitive measure of catalyst performance than using the absolute pressure recorded for each run.

An example of the results gathered is shown in Figure 1. This shows the relative pressure and temperature results for 5% platinum on alumina. Initially, there is a drop in the relative pressure below zero. This is due to the HTP having a much higher density than the nitrogen gas injected in the datum run, resulting in a reduced rate of pressure rise within the reactor. Once hydrogen peroxide decomposition initiates there is a significant rise in both the relative reactor pressure and temperature; in the majority of cases both the temperature and pressure reach peak values within the first 20s of the experiment. Thereafter, both the temperature and pressure tend to decay. This is undoubtedly due to the combined effects of thermal capacity and condensation of the steam generated by the reaction. The temperature profile does show some erratic behaviour. This is most likely due to localised affects at the tip of the thermocouple used to measure the temperature of the decomposition products.

The trend in relative reactor pressure is similar for both the ceramic pellet and metallic foam-based catalysts. Only the reaction with 0.5% palladium on alumina catalyst fails to reach completion within 60s, with the reactor pressure still rising, albeit at a slower rate. The temperature profiles show a slightly more erratic behaviour, although a general trend of a rapid temperature rise followed by a slower rate of temperature decay was observed.

The performance of the metallic gauzes was generally disappointing. In all but two cases the decomposition either failed to initiate or was quickly quenched; this led to a negligible temperature and pressure rise. The only exceptions to this were the heat-treated platinum/iridium gauze and the silver gauze. The results for the silver gauze are shown in Figure 2. A smaller initial pressure drop can be seen due to the lower delivery pressure. This leads to a longer injection time and results in a smaller difference between the datum and live runs. Once the decomposition had begun the temperature rapidly rose to a peak temperature of 133 deg C. As the reactor cooled the steam condensed on the cold reactor walls and relative reactor pressure fell slightly before remaining constant for the remainder of the run. Note that, unlike the pellet-based catalysts, there was a significant delay before the reactor pressure and temperature increased.

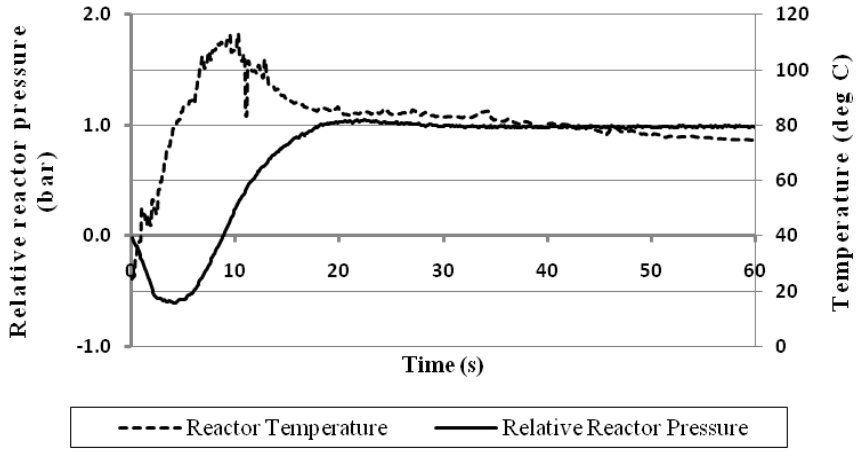


**Figure 1: Sealed reactor results for 5% Platinum on Alumina**

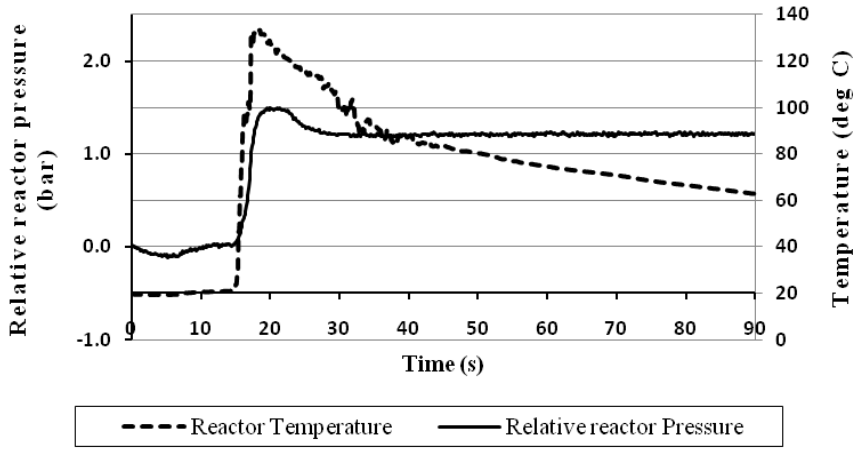


**Figure 2: Sealed reactor results for silver gauze**

Due to the different injection processes it was not possibly to directly compare the pellets and foams with the metallic gauzes. The results gathered can be interpreted in a number of ways; however this apparatus was designed to specifically investigate initial performance. Accordingly, four parameters relating to the rate at which the temperature rises and to the peak temperatures and pressures measured were used to assess performance [8]. Table 3 is a list of the most and least desirable catalysts that have been identified as a result of testing in this apparatus using these criteria. At this time batches 006-009 have not been tested within this apparatus.

**Table 3: Summary of catalysts tested using the sealed reactor**

| Most Desirable Catalysts | Least Desirable Catalysts |
|---|---|
| 0.5% Platinum on alumina | 0.5% Palladium on alumina |
| 1% Platinum on alumina | Batch 001, 003 |
| 5% Platinum on alumina | Palladium/nickel gauze |
| 0.5% Ruthenium on alumina | Platinum gauze |
| 2% Ruthenium on alumina | Platinum/iridium gauze |
| Batch 002, 004-006 | Platinum/iridium/rhodium gauze |
| Batch 100-102 | Heat-treated palladium/nickel gauze |
| Silver gauze | Heat–treated platinum gauze |
| Heat-treated platinum/iridium gauze | Heat-treated platinum/iridium/rhodium gauze |
| | Heat-treated silver gauze |

## 4. Lifetime Mass-loss assessment

Initial down selection has been completed utilising the sealed reactor. However the sealed reactor is not sensitive enough to differentiate between many of the high-performing ceramic pellet-based catalysts. In addition to this, the sealed reactor makes no attempt to assess lifetime or survivability. Accordingly a second set of apparatus has been designed to further assess these qualities. To maximise the effectiveness of this rig it is both simple and open, allowing the operator to visibly assess the catalyst's performance qualitatively as well as acquiring data for later quantitative analysis.

The apparatus consists of a round bottomed flask into which is placed ten grams (± 0.02g) of 87.5% hydrogen peroxide as measured by a mass balance accurate to 0.01g. A thermocouple is also placed within the flask so that its tip lies within the pool of hydrogen peroxide. In all cases the start temperature of the experiment was controlled to within 1 deg C of a nominal 22 deg C. A timer was initiated when a catalyst sample, of known dimensions, was added to the flask. The result was an increase in peroxide temperature and a reduction in mass as steam and oxygen were generated and allowed to escape. The temperature and mass of the hydrogen peroxide was recorded for later analysis using National Instruments' LabVIEW software.

The experiment was considered to have concluded when one of two criteria was met. The first was whether 90% of the original mass had been lost due to the formation of decomposition products. The target of 90% mass loss was chosen to allow for the added weight of the catalyst and any small droplets of peroxide or water that had condensed around the mouth of the flask and were, therefore, no longer in intimate contact with the catalyst. The second criterion was a time limit of 600s: the experiment was stopped after this time regardless of whether or not the 90% mass loss criterion had been met. After the experiment was completed the catalyst material was removed and allowed to cool in a clean container.

The lifetime of the catalyst was assessed by repeating the above experiment with the same sample of catalyst material until either a run limit of 10 had been reached or the catalyst failed to decompose 10% of the original mass in 600s. If the latter occurred the catalyst was assumed to be exhausted. After each run the catalyst would be visually inspected to identify if any structural degradation had occurred; if found, the catalyst was rejected from any further testing.

The results of the sealed reactor ranking indicate that the majority of the metallic gauze catalysts do not perform well. Accordingly these have been rejected from further testing. Only silver and heat treated platinum-iridium showed significant catalytic properties. However, in the form tested, heat treated platinum/iridium was structurally too weak to undergo further testing and was therefore also rejected.

### 4.1 Lifetime Mass-Loss Results

To date 12 ceramic pellet-based catalysts and 3 metallic foam-based catalysts have been assessed. Only three catalysts completed all 10 runs; 5% platinum on alumina, Batch 005 and Batch 101. All the others either structurally failed or were exhausted within the 10-run limit. Figure 3 and Figure 4 show the results for runs 1, 5 and 10 using 5% platinum on alumina. Figure 3 provides percentage mass change results while Figure 4 shows the temperature profiles. It can be seen that the temperature fails to surpass 120 deg C, which is a common trend in all the tests conducted. This is due to the thermocouple detecting the boiling point of the peroxide solution rather than the much higher gas temperature. The temperature profiles do show some erratic behaviour in the later part of the experiment; this is due to the catalyst moving around within the peroxide solution, causing local temperature fluctuations at the thermocouple tip. With every run the performance of the catalyst decreases, as indicated by the reduction in the percentage of hydrogen peroxide successfully decomposed within the 600s time limit. The rate of mass change tends to accelerate once the temperature of the liquid solution exceeds 100 deg C; this is due to the liquid water turning to steam and being expelled alongside the gaseous oxygen.

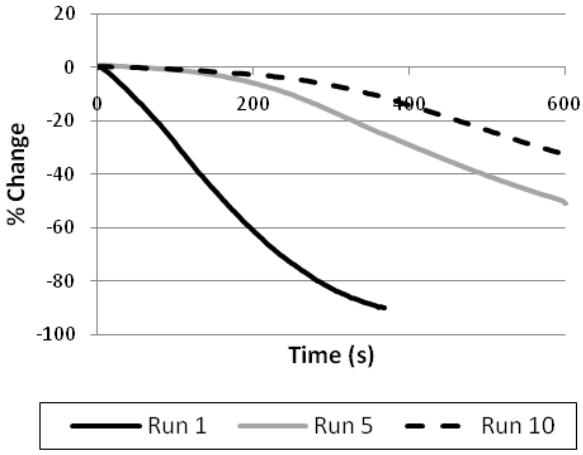


**Figure 3: Percentage mass change - 5% Platinum**

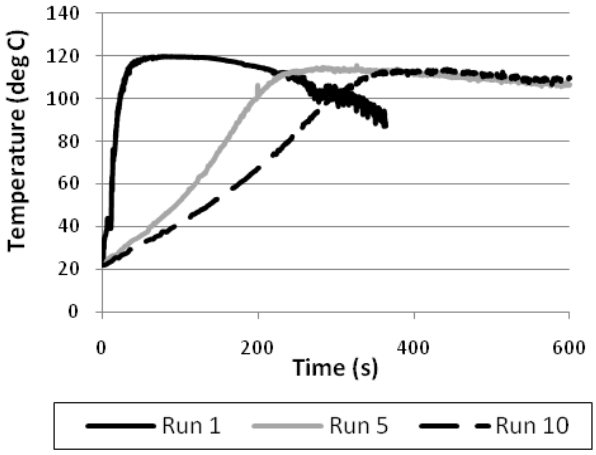


**Figure 4: Temperature Profile - 5% Platinum**

Decreasing performance with repeated immersions of the catalyst can be identified in all of the experiments. In several cases there was a rapid loss in performance; this is most obviously seen with 0.5% ruthenium on alumina as shown in Figures 5 and 6. In this case the first run performance was good but by the second run the performance had significantly degraded with a percentage mass loss of only 1.2% and only a small increase in temperature throughout the run.

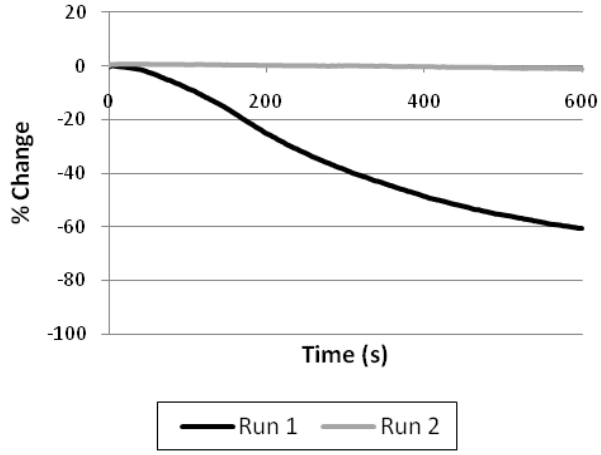


**Figure 5: Percentage mass change - 0.5% Ruthenium**

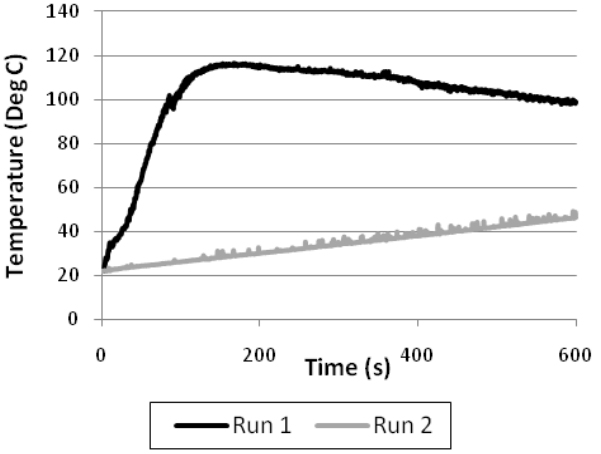


**Figure 6: Temperature Profile - 0.5% Ruthenium**

Thankfully this level of catalyst degradation was rare. The results for 0.5% ruthenium were verified in a monopropellant thruster test firing, which showed significant catalyst degradation over four test runs. Initial performance provided temperatures over 600 deg C in the nozzle; however by run four liquid peroxide was seen to be expelled.

The current test apparatus also provided insight into catalyst survivability. Whereas for the sealed reactor it was difficult to identify if catalyst damage was a result of exposure to hydrogen peroxide, this was not the case with the lifetime mass-loss rig. In several cases very high performing catalysts were seen to fail structurally very quickly, presumably due to the combined effects of thermal and chemical shock. This was particularly apparent with 2% ruthenium on alumina and batch 102. Both these catalysts showed excellent reactivity, with complete decomposition of the peroxide occurring in less than 40s in the first run and an almost equivalent performance in run 2. However, in both cases the catalysts had disintegrated and therefore failed structurally by run 3. Unfortunately this meant it was not possible to assess catalyst lifetime, especially for the 2% ruthenium on alumina which, unlike 0.5% ruthenium on alumina, had not shown signs of exhaustion.

Three parameters have been used to assess the catalysts tested within this apparatus. They each focus on one particular aspect of performance; mechanical integrity, lifetime and initial performance. The first criterion was

mechanical integrity: if the catalyst was shown not to be able to remain intact after repeated immersions in hydrogen peroxide, it was rejected from further assessment. The second was lifetime; the catalysts were ranked according to how many runs were successfully completed. The final criterion was run 1 performance. A linear trend line was placed over the run 1 data and the gradient of that line recorded. To allow for differing catalyst sizes, this value was then divided by the Euclidean surface area in millimetres. The results of this assessment are shown in Table 4, at this time batches 001-003 and silver gauze have yet to be tested.

**Table 4: Lifetime mass-loss results**

| Catalyst Name | Mechanical Integrity | No. of Runs to <10% Mass loss | Normalised Av. Gradient Run 1 |
|---|---|---|---|
| 0.5% Palladium | ✓ | 1 | -8.77E-05 |
| 0.5% Ruthenium | ✓ | 2 | -2.10E-03 |
| 2% Ruthenium | × | | |
| 0.5% Platinum | ✓ | 7 | -3.19E-03 |
| 1% Platinum | ✓ | 6 | -2.90E-03 |
| 5% Platinum | ✓ | >10 | -5.24E-03 |
| Batch 004 | × | | |
| Batch 005 | ✓ | >10 | -8.76E-02 |
| Batch 006 | × | | |
| Batch 007 | × | | |
| Batch 008 | × | | |
| Batch 009 | × | | |
| Batch 100 | × | | |
| Batch 101 | ✓ | >10 | -3.19E-02 |
| Batch 102 | × | | |

The results have been ranked in order, where 1 is high (indicating desirable reactivity properties) and 7 is low. At the present time no particular weighting has been assigned to any one of these parameters. However, the overall score is the summation of each individual value squared. This provides a more accurate ranking method. Table 5 shows the catalyst listed in order of reactivity from highest to lowest.

**Table 5: Resultant ranking for lifetime mass-loss results**

| Catalyst Name | Mechanical Integrity | No. of Runs to <10% Mass loss | Normalised Av. Gradient Run 1 | Overall Score |
|---|---|---|---|---|
| Batch 005 | 1 | 3 | 1 | 11 |
| Batch 101 | 1 | 3 | 2 | 14 |
| 5% Platinum | 1 | 3 | 3 | 19 |
| 0.5% Platinum | 1 | 4 | 4 | 33 |
| 1% Platinum | 1 | 5 | 5 | 51 |
| 0.5% Ruthenium | 1 | 6 | 6 | 73 |
| 0.5% Palladium | 1 | 7 | 7 | 99 |

The results indicate three catalysts in particular that should be taken forward for further investigation. These catalysts, batch 005, batch 101 and 5% platinum on alumina, showed not only good performance but also a significant lifetime as well as good structural integrity.

## 5. Conclusions

Two experimental rigs have been developed and used to assess the performance of heterogeneous catalysts for the decomposition of high concentration (87.5%) hydrogen peroxide. The first is a sealed reactor rig, which was designed to capture the initial reactivity characteristics of the catalysts. The results of the tests using this rig show similarities with the work undertaken in [9]. The sealed reactor did identify both good and poor performing catalysts. It was found that many of the metallic gauzes failed to decompose the peroxide, with only two gauzes showing any significant catalytic properties.

The second rig, the lifetime mass-loss apparatus, has been used to provide additional data on structural survivability and lifetime as well as performance. Some experiments remain outstanding and will be conducted during the next phase of testing. This apparatus did identify structural integrity issues with many of the catalysts manufactured in-house; however those that did survive the testing procedure were shown to have excellent performance.

Batch 005, batch 101 and 5% platinum on alumina in particular were identified as having promise and will now be taken forward and tested within an instrumented catalyst bed. This will allow a more detailed study of the catalysts to be undertaken at conditions more representative of real operation.

## Acknowledgments

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement number 218819.

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