

**Environmentally-Preferred
Advanced Generation**

Durability of Catalytic Combustion Systems

APPENDIX V: Catalyst Materials Development

Gray Davis, *Governor*



RESOURCES AGENCY

**November 2001
CALIFORNIA
ENERGY
COMMISSION**

CALIFORNIA ENERGY COMMISSION

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**CATALYTICA ENERGY
SYSTEMS
Mountain View, CA**

Contract No. 500-97-033

Contract Amount: \$1,316,030

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Preface

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Commission), annually awards up to \$62 million to conduct the most promising public interest energy research by partnering with Research, Development, and Demonstration (RD&D) organizations, including individuals, businesses, utilities, and public or private research institutions.

PIER funding efforts are focused on the following six RD&D program areas:

- Buildings End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Strategic Energy Research.

What follows is the topical report for the Durability of Catalytic Combustion Systems Project, conducted by Catalytica Energy Systems. The report is entitled “**Catalyst Material Development**”. This project contributes to the Environmentally-Preferred Advanced Generation program.

For more information on the PIER Program, please visit the Commission's Web site at: <http://www.energy.ca.gov/research/index.html> or contact the Commission's Publications Unit at 916-654-5200.

I. Background and Objectives

A key technical materials issue affecting the operability and lifetime of combustion catalysts is the thermal stability of the washcoat-catalyst system. The washcoat-catalyst is a porous layer of a ceramic oxide applied to the thermally conductive high-strength metal foil that serves as a support. Catalytically active metals and oxides, in our case platinum group noble metals (PGM), are dispersed within the porous washcoat layer. The thermal stability of the washcoat material is typically expressed as loss in the washcoat surface area with time at the operating temperature and conditions of the catalyst in the engine. Previous exploratory work performed at Catalytica Energy Systems, Inc. (CESI) identified several washcoat materials with substantially better thermal stability than the current formulation. The superior sintering resistance (more correctly described as coarsening resistance) of the new material is shown by its substantially higher surface area compared with CESI's standard stabilized support and a commercial non-stabilized supporting oxide, zirconia, after 75-hours exposure to humid air (~10-vol% added water vapor) at elevated temperature.

Catalyst Formulation	Catalyst Description	BET* Area fresh (m ² /g) calcined in air 1000°C	BET* Area aged (m ² /g) 10-vol% H ₂ O 1035°C
CESI standard hot-stage catalyst	stabilized supporting oxide	41	1.9
Developmental material CEC/CESI	tantalum-zirconium oxide support	28	15
Zirconia reference	commercial zirconia oxide support	7	4.3

* Brunauer, Emmett, and Teller --- the developers of the surface area measurement technique

Table 1.1 -- Thermal sintering data comparing the loss in surface area of the current ceramic washcoat material with a new high thermal stability material

These data show that the tantalum-zirconia developmental washcoat material may provide substantially improved performance for the catalyst under the operating conditions of the catalyst in a gas turbine, 900 to 1000°C with higher levels of water vapor. However, several issues need to be resolved before this material can be used in an engine combustor:

- Commercially viable processing. The preparation procedures for the washcoat ceramic material have only been developed for small scale (1 to 2 grams) and need to be scaled to 500 to 1000 grams to prepare enough material for detailed and large scale testing.
- Thermal stability of catalysts. Long term laboratory aging tests should be performed to evaluate the stability of the new washcoat material and of supported noble metal catalysts prepared with the new material.
- Application and adhesion to foils. There is a need to develop procedures to apply the new material to the substrate foils and to achieve the required adhesion and washcoat strength.

The specific objectives of each of the six proposed subtasks are described below with a description of the work performed. Major efforts were expended on the preparation, aging, and

sub-scale performance testing of combustion catalysts using the new washcoat material. In summary, these subtasks were performed successfully, and the preparation of high quality ceramic powders was scaled-up and the combustion activity of catalysts prepared from these materials exceeded our expectations. But, the long-term aging tests showed that the ultimate long-term performance of these promising catalysts were comparable if not inferior to our current formulations. Less than expected efforts were expended on the development of procedures for bonding the new materials to substrate foils and testing adhesion (Task 5.4) for two reasons. Relatively simple modifications of slurry formulations proved adequate early on and the results of the aging investigations indicated that full-scale testing at Silicon Valley Power was not warranted.

Another area of concern expressed in the CEC Pier I proposal under the heading of catalyst materials is the selection of the corrugated metal foil that forms the base for the monolithic catalyst structure. Substrate foils for high temperature catalysts comprised of the new washcoat material should use a high strength high temperature foil alloy. At the time of the proposal, CESI used a FeCrAl alloy in all monoliths, but this alloy has limited tensile strength at high temperature. Improved performance and longevity can be obtained. Substrate foil should possess a longer creep life and a lower oxidation rate. Since that time CESI, by using a NiCrAl alloy, has gained considerable experience in the pretreatment and application of washcoat materials to such corrugated NiCrAl foils; and catalytic combustion tests have shown good performance. Fundamental measurements of the oxidation rates and creep resistance of the base and pretreated NiCrAl foils were performed under the CEC Pier I program. These investigations focused on the use of thicker foils (10-mil vs. 2-mil in catalyst monoliths) as an axial support material. The results of the materials studies in the axial support work can be used to describe performance of monolith foils as well, and additional tests were not conducted as part of Task 5.

II. Production of Test Quantities of New Ceramic Materials (Task 5.1)

The new material was prepared previously by a sol-gel process. Sol gel chemistry involves the slow hydrolysis of metal alkoxide reagents in very dilute alcohol solutions. Careful mixing and supercritical drying are typically required. This process limits the quantity of highly porous solid that can be prepared in a given size vessel. Under Task 5.1, several new chemical approaches that are readily adapted to larger scale processing were evaluated to obtain the desired ceramic material.

The specific work objectives for this task were:

Subtask 5.1.1 Evaluate three (and additional, if needed) new chemical approaches to the production of the developmental washcoat material.

Subtask 5.1.2 Prepare test quantities of the ceramic material, approximately 500 to 1000 g.

These objectives were fully met as described below.

2.1 Evaluation of hydrolysis and precipitation processes (Task 5.1.1)

Molecular-scale homogeneity of the two metal components is thought to be the primary source of the exceptional surface stability in the previously prepared Ta-Zr aerogels. Slow hydrolysis,

under acidic or basic conditions in dilute solutions typically produces a clear gel; while rapid hydrolysis in concentrated solutions under neutral conditions typically produces a cloudy (heterogeneous) suspension. A preliminary precipitation experiment was performed (using conditions and starting reagents similar to the aerogel preparation) to produce what was expected to be a mixed phase of the two oxide precipitates. This heterogeneous material was intended to validate the technique of producing homogeneous material by the aerogel method. After oven drying and calcination, the precipitated Ta-Zr mixed oxide showed a homogeneous crystalline phase as determined by x-ray diffraction (XRD) analysis. It also showed a specific surface area equal to sol gel preparations that were also oven dried (xerogels) and approximately half of the best aerogel preparation. Since near homogeneity apparently was achieved with this simple precipitation technique, we investigated changes to the conditions of the precipitation method to enhance the initial surface areas of the homogeneous precipitate. Reaction parameters such as water concentration, acid and base catalysts were manipulated to explore the effect of these parameters on surface area stability.

Effect of H₂O concentration and the effect of acid/base catalysis

For a typical non-catalyzed 20-mol% tantalum-zirconia co-precipitate synthesis, 10 ml H₂O (10X stoichiometric) was added to 100 ml¹ of anhydrous 1-propanol. Next, in a nitrogen-purged glove box 1.6 gm tantalum ethoxide and 8 gm zirconium n-propoxide (70-wt% in n-propanol) were mixed in 50 ml anhydrous 1-propanol. This mixture was removed from the glove box and added to a 25-ml separatory funnel. The tantalum-zirconium solution was added to the water-alcohol solution, at a rate of 2 drops per minute with vigorous agitation. The resulting fine white precipitate was filtered in a Buchner funnel with #200 cellulose filter paper, washed twice with 100 ml aliquots of distilled and de-ionized water, and then washed with 100 ml ethanol (Aldrich, anhydrous). The wet precipitate was then dried at 110°C overnight. The dried white powder was ground with a mortar and pestle and calcined at 1000°C for 10-hrs. Table 2.1.1 lists the parametric changes to the above method including varying the amount of water and acid/base catalysts.

Run #	H ₂ O X stoichiometry	μL conc. HNO ₃	μL conc. NH ₄ OH	SA 1000°C (m ² /g)	SA 1035°C in moist air (m ² /g)
1020-105-1	10	-	-	20	10.2
1020-105-2	10	375	-	12	5
1020-105-3	10	-	375	13	-
1020-105-4	3	-	375	20	-
1020-105-5	5	-	-	12	-
1020-105-6	20	-	-	20	-
Aero gel std.	3	375	-	28	15

Table 2.1.1 -- Effect of hydrolysis stoichiometry and acid or base addition on the preparation of precipitated Ta-Zr oxide powders.

¹ Initially, 50 ml of alcohol was added to the water solution. Half way through the alkoxide addition, 50 ml was added due to thickening.

The total specific BET (N₂) surface area measurements for the precipitates (runs 1020-105-1 through 1020-105-6) following calcination in ambient air at 1000°C and humid air at 1035°C (Table 2.1.1) lead to the following conclusions:

- The water adjustment had the biggest effect on resulting surface area.
- Neither acid nor base catalysis is necessary.
- The best-precipitated materials maintained surface areas within 25 percent of the measured surface area of the aerogel catalyst.

The high surface area precipitates exceeded the surface area measured for xerogels after 1000°C calcination (previously, xerogels have been shown to be homogeneous by XRD).

If homogeneous mixing is achieved during precipitation, then the drying step must be an important factor in the initial surface area after calcination. We concluded that further improvement in the mixing step for larger batches of reagents coupled with changes in the drying step should produce materials that have initial specific surface area approaching the aerogel standard.

Precipitation by microfluidization

Differences in relative condensation rates of the two metal alkoxides necessitate rapid mixing to create a fine-grained co-precipitate. Microfluidization introduces sub-microsecond mixing through a micro orifice. Initial experiments were conducted using a dual chamber (Microfluidics) microfluidizer designed by Catalytica's Advanced Technologies program.

The mechanical operation of the microfluidizer requires that each chamber maintain an equal amount of liquid. Therefore, adjustments were made to the separate solutions of water and alkoxide mixture while keeping the relative ratios of the components constant. In addition, the tantalum concentration was increased from 20 to 25 mole percent. This increase was based on our previous aerogel research that showed that the minimum amount of tantalum necessary for surface stability was 20 mole percent, and a maximum was reached at 30 mole percent.

For hydrolysis, 75 ml H₂O was added to 450 ml of anhydrous 1-propanol in a nitrogen-purged glove box. This solution was removed from the glove box in a sealed bottle. Both holding chambers of the microfluidizer were filled with ~500 ml of isopropanol and the machine was flushed twice. The machine was then flushed with an additional 800 ml of 99.95% isopropanol and drained. The alkoxide mixture was added to the nitrogen-purged chamber 1 and the hydrolysis mixture was added to chamber 2. The two mixtures were pumped through the 30µm orifice with a fore-pressure of approximately 15,000-psi. The entire mixing and hydrolysis process took less than 2 minutes at a flow rate between 500-600 ml per minute. The temperature of the recovered liquid peaked at ~35°C. A suspension of fine white precipitate was formed and transferred into a 1-liter Nalgene polypropylene bottle. The liquid-precipitate was centrifuged at 2500-rpm for 5 minutes and the clear solvent decanted until approximately ~1/3 of the initial mixture remained.

Effect of drying technique

The method used to remove the solvent from the precipitate could be a factor in stabilizing the initial surface area. Reducing the amount of surface tension and partial pressure in the interstitial pores can help to maintain the integrity of these pores and increase the surface area of the dried powder. Vacuum drying and supercritical drying (SCD) could help to maintain surface area. Two drying experiments were performed to assess the effectiveness of these techniques.

The precipitate paste from an original 200-ml aliquot of the microfluidized product was washed twice with 100 ml of anhydrous n-propanol, and then 50 ml more of n-propanol was added. The precipitate solution was then transferred to a 250 ml round bottom flask. The flask was placed on a rotary vaporization system (“rotovap”). The rotovap spun at 5-6-rpm with a vacuum pulled to a pressure of 8.2 Torr. The rotovap bath was maintained between 45-55°C. The dried material was allowed to dry then held in the warm bath under vacuum for an additional hour.

For supercritical drying, about 350 ml of the precipitate solution was placed in a 1-liter glass liner and placed in a 1-liter autoclave. The high-pressure system was flushed with nitrogen and then sealed. The critical properties of 1-propanol are $V_c = 120$ ml/mol, $T_c = 536$ K, and $P_c = 52$ atm. The vessel was heated at a ramp rate of 3°C/min to 573 K while maintaining a pressure of about 1000 psig. The autoclave was kept at the final temperature of 295°C for 15 minutes to ensure thermal equilibrium. The pressure was then released at a rate so that about 10 ml of solvent condensed per minute. The autoclave was then purged with $N_2(g)$ and cooled.

Upon completion of the two drying experiments, 2-gram samples of each of the white powders were calcined at 1000°C for 10-hrs. The resulting crystalline solid powders were submitted for total surface area analysis by BET (N_2) physisorption (Table 2.1.2). The supercritically dried material was additionally calcined at 1035°C in humid air (10-vol% H_2O) for an additional 75-hrs.

Dried Sample	1000°C/10-hrs with ambient air SA	1035°C/75-hrs with 10% H ₂ O SA
Vacuum dried 886-147-1	21 m ² /g	---
Supercritically dried 886-147-2	26 m ² /g	13.5 m ² /g

Table 2.1.2 -- BET Surface area results for dried Ta-Zr oxide materials

The results show that the drying step does play a role in producing materials with relatively high initial surface areas. The supercritically dried material after calcination at 1000°C has a surface that is at least 25% greater than oven or vacuum dried material. The results for the supercritically dried powder after 1035°C calcination in humid air are comparable to our best aerogel material with similar composition.

The results for the precipitated Ta-Zr mixed oxide were conclusive and indicate that precipitates produced by microfluidization are superior to those precipitates produced by the drop method after 1000°C calcination. The microfluidization technique is therefore a viable alternative to slow mixing methods with the additional advantage that mixing and hydrolysis time is shortened by an order of magnitude. Thus the microfluidized, supercritically drying preparation technique was selected for production of a large batch of the new washcoat material to be used in subsequent testing.

2.2 Large scale preparation of washcoat material for sub-scale testing (Task 5.1.2)

Precipitate preparation

The procedure for the large-scale preparation of 25-mole% Ta-Zr mixed oxide followed closely that described above for the microfluidization-hydrolysis and supercritically drying preparation. Scale-up was targeted at approximately 250 grams of calcined material. Following are procedures for the prepared material:

Mixing – For the hydrolyzing mixture 672-g of water was added to 4 liters of n-propanol. For the alkoxide mixture, 138-g tantalum ethoxide and 480-g zirconium n-propoxide (70-wt% in n-propanol) were added to 4-liters anhydrous 1-propanol in a nitrogen-purged glove box and placed in sealed 2-liter bottles. The bottles were shaken to blend the alcohol-alkoxide mixture. The microfluidizer was flushed with 500-ml anhydrous n-propanol before adding the two mixtures. The alkoxide chamber was purged with N₂ while processing. The approximate 150-ml hold up of each solution was flushed with 150 ml of anhydrous n-propanol. The entire mixing/hydrolysis process was completed within approximately 15 minutes.

Centrifugation, Drying, and Calcination – The centrifugation step consisted of adding approximately 750 ml each of the precipitate suspension to four 1-liter Nalgene bottles, spinning the suspensions at 2300 rpm for 5-6 minutes, then decanting the clear solvent. The collected paste was scraped from the bottles and collected in beakers. Next, about 325 ml of paste (the solid was estimated to occupy no more than 5% of this volume) was added to the 1-liter glass autoclave liners. Each of some 12 batches was supercritically dried as described above. The total collected weight of washcoat after drying was 262 grams. The entire batch was calcined at 500°C for 10-hrs.

Toll processing

The supercritical drying step of the chosen precipitation process was clearly the slow processing step and required many batches for even 250-gms of powder. An alternative to neat supercritical drying, i.e., solvent only with no added drying fluid, is drying with supercritical CO₂. This drying step can be conducted semi-batch at lower temperatures in flowing supercritical CO₂. Applied Separations was contracted to process another batch of 4-liters of Ta-Zr oxide paste following microfluidization/hydrolysis and centrifugation as described above.

Applied Separations prepared eight small (~10-gm) samples of dried powder from the paste for various combinations of drying temperature (100 to 250°C), pressure (2000- and 5000-psi), and drying time (2- to 8-hr). The BET surface area for these samples following calcination at 1000°C varied from about 10 to 20-m²/gm. The best results were obtained for samples that were heated to the highest temperature before depressurizing the drying vessel. A two-stage drying process was chosen because of the limited temperature range of Applied Separations' commercial-scale (10-L) drier. The large batch was dried with supercritical CO₂ at 150°C in the large-scale drying vessel for 4-hours. The partially dried and compact solid was then supercritically dried to 275°C. The solid yield was about 500-gm and the BET surface area of a representative sample showed 18-m²/gm after calcination at 1000°C. Unfortunately, a series of delays in the drying operation prevented CESI from using this toll processed material in the long-term aging reactor and sub-scale tests. It was retained for additional tests and for production of a full-scale engine test if needed.

III. Develop Coating Procedures (Task 5.2)

Each ceramic washcoat oxide requires a specific formulation and pretreatment condition to bond the applied washcoat layer. CESI's current washcoat slurry formulation contains a dispersing

agent, a binding agent and a porosity-enhancing agent. The dispersing agent keeps the agglomerated particles separated and suspended in the aqueous liquid, the binding agent bonds the washcoat to the underlying pretreated foil scale, and the porosity enhancing agent facilitates the penetration of the washcoat layer for the natural gas fuel. This task was proposed to allow the possibly lengthy search for a thermochemically compatible binding agent and calcining conditions for bonding and testing the adherence and coherence of the washcoat layer. CESI has developed a “Washcoat Abrasion” test that can quantify the cohesion and adhesion properties of the washcoat applied to a corrugated metal foil.

The specific work proposed for this sub-task was:

- 5.2.1. Using the research catalyst production system at CESI’s Mountain View facilities, prepare test samples of coated foil. These test samples are typically 2 to 3 meters length of coated foil. It is envisioned that 10 to 20 test samples may be prepared to fully develop the coating process. These samples will be processed in the same manner as the typical engine catalyst.
- 5.2.2. Evaluate the test samples with “Abrasion Test Procedure”. As needed, prepare epoxy mounted and sectioned samples for Scanning Electron Microscope (SEM) analysis.

3.1 Monolith preparation procedure (Task 5.2.1)

CESI has much previous experience in bonding washcoat to pretreated foils. A test was performing by an outside service to determine the “zero-point charge” for aqueous suspensions of the new Ta-Zr oxide powders. The powder had been calcined at 1000°C and extensively ball-milled using standard CESI procedures. Zeta potential measurements showed that the zero point charge on the suspended particles occurred at a higher pH than with CESI’s standard washcoat powder, making it easier to maintain the suspension.

Washcoats were prepared on FeCrAl foil using the standard formulation and coating process parameters. A mixture was made of two Ta-Zr oxide powders of the same composition; but, one with 85-wt% calcined in air for 10-hours at 950°C and the other 15-wt% calcined at 500°C. Two coated foils were prepared using the standard formulation and found to have unacceptable adhesion. For a third preparation 5wt% colloidal ZrO₂ was added to the powder mixture with the binding agent to improve adhesion. Additional water and acid were added to decrease the viscosity of the resulting slurry. The slurry was dispersed in an ultrasound bath for 15-30 minutes prior to application rather than the typical ball-milling procedure. The slurry was applied to the catalytic foil and found to have acceptable adhesion and cohesion. This simple modification of the bonding formulation and post-coating treatment was adapted for the production of monoliths for sub-scale testing under Task 5.4.

3.2 Abrasion tests (Task 5.2.2)

Washcoats composed of the new material were not applied to the NiCrAl foil nor were adhesion tests performed for the FeCrAl coated foils. After the CEC proposal was written but prior to the start of Task 5.2, CESI had fully established a coating process for the NiCrAl using our standard washcoat. Given the experience in developing processes for producing adequate bonding with standard washcoat on NiCrAl foil and the Ta-Zr washcoat on FeCrAl, CESI is confident that adequate bonding would be achieved with the new washcoat material on pretreated NiCrAl foils.

The CESI abrasion test and another method of directly observing the washcoat foil interface, i.e., washcoated foil pieces mounted in epoxy and sectioned for SEM (scanning electron microscopy) observation, were available as proposed, but judged not necessary to develop an adequate washcoat bonding process. Instead, attention was focused on the prospects for improved catalyst stability with the developmental ceramic supports.

IV. Thermal Stability Testing of New Catalyst Materials (Task 5.3)

The thermal stability of catalysts is a critical property that governs the useful life of a combustion catalyst module in operation. CESI has developed a system of four high pressure (used to 20-atm), high temperature (used up to 1010°C), isothermal reactors (see Figure 4.1) that exposes catalytic foils, washcoat powders, and component powdered materials to a simulated combustion environment for long time periods (up to 8000-h). The environment within the vessel reproduces the typical gas composition (including oxygen, water vapor, and even trace sulfur oxide present) within the washcoat of a gas turbine catalyst module. The differences between the simulated and the engine environment, i.e., the lower gas flow rate and the lack of thermal gradients caused by the combustion of fuel, are not considered significant. Samples of catalysts used in engine tests (2900-hr) have specific surface areas and specific amounts of exposed noble metal (the active component in combustion catalysts) that follow the values expected from the HPAR tests. These reactors were used to examine the thermal stability of the new Ta-Zr oxide washcoat materials.

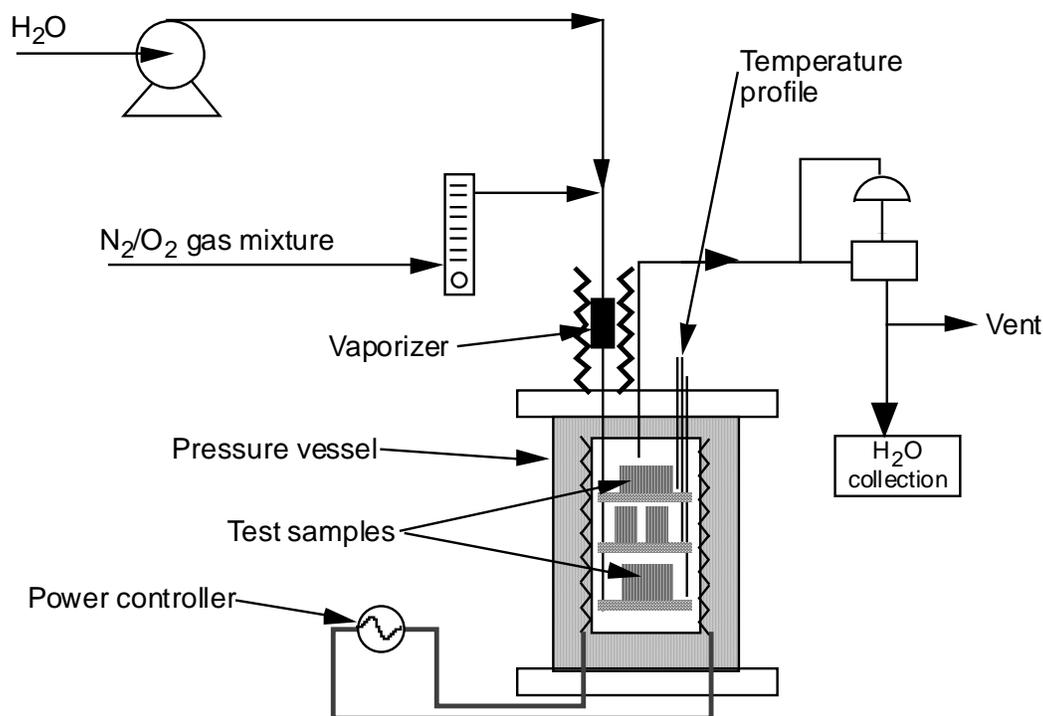


Figure 4.1 -- High Pressure Thermal Aging Facility that reproduces the pressure, gas phase composition and temperature of the actual gas turbine combustor

The specific set of subtasks is:

- 5.3.1. Prepare test quantities of new ceramic washcoat powder that was used in the preparation of catalyst powders and pretreated in a manner similar to the target commercial catalyst foils.
- 5.3.2. Prepare catalyst coated metal foil samples pretreated in a manner similar to the target catalyst. The metal substrate foil in this case was to be a NiCrAl superalloy.
- 5.3.3. Age the above samples in the high-pressure aging reactor (HPAR) system at the expected conditions of operation in the gas turbine combustor
- 5.3.4. Remove samples periodically and characterize these samples for total washcoat surface area and specific surface area of the active catalyst component (exposed platinum group metal, PGM).

These tasks were completed successfully as described in the following sections with the exception that the metal foil catalyst materials were coated over the FeCrAl foil and then scraped from the foil following final treatment and aged as a powder. Table 4.1 lists the different types of catalyst aged in both the 900°C and 975°C HPAR tests.

Washcoat material	Catalyst form	Final calcination temperature, time	HPAR temp 900°C	HPAR temp 975°C
Std supporting oxide	powder	1000°C, 10 hours	X	X
Std supporting oxide	monolith	950°C, 10 hours	X	X
Ta-Zr oxide	powder	1000°C, 10 hours	X	X
Ta-Zr oxide	monolith	1000°C, 10 hours		X

Table 4.1 -- Catalysts tested in HPAR experiments at 900°C and 975°C

4.1 Preparation of powdered catalyst samples (Task 5.3.1)

Both hand-prepared catalyst powders and powders scraped from catalyst coated foils prepared by CESI's prototype catalyst manufacturing line were inspected for long-term thermal stability. Our standard commercial catalyst washcoat powder and the initial batch of the new Ta-Zr oxide washcoat powder as described above for Task 5.2.1 were used in preparing standard PGM catalysts. The powdered catalysts were prepared by hand impregnation of PGM salts using the incipient wetness technique, e.g., just enough liquid was used to wet the powder. The salt impregnated powders were then dried and calcined following the standard procedures developed for washcoated foils.

4.2 Preparation of catalyst samples scraped from coated foils (Task 5.3.2)

The CESI standard catalysts were scraped from washcoated activated catalyst foils. The new washcoat powders were used in the preparation of standard foils with some modification of the washcoating formula and calcining procedure. As discussed above, additional binding agent was required in the slurry and a higher calcining temperature was used for the new Ta-Zr oxide washcoat material. Other than those modifications, the foil preparation and catalyst coating procedures were the same as for the standard catalysts. The final calcining temperatures to generate the "fresh" samples are shown in Table 4.1; the exposure time was 10 hours in all cases.

Powdered samples of the calcined foils were collected after scraping the foil with a wire brush. These powdered samples were then aged in the HPAR tests along with the hand-prepared powdered catalysts.

4.3 HPAR aging of CESI standard and new Ta-Zr oxide catalyst samples (Task 5.3.3)

Two separate tests were performed under two different temperatures, 900°C and 975°C both at a pressure of 10 atmospheres. The catalyst powders were loaded into ceramic crucibles for ease of sampling and placed in the HPAR. After each time interval, the crucibles were removed from the reactor, and a portion of the catalytic material was removed for analysis. The portions (~1-gm each) of each powder were characterized at progressive intervals from 4 to 8000 hours for the 900°C run and from 30 to 4000 hours for the 975°C run. The specific BET (N₂) surface area and the amounts of active PGM (via H₂ titration following reduction) were measured for each sample as shown in the following table and figures.

900°C HPAR results

The results for 900°C HPAR tests (Table 4.3.1) show that catalysts prepared from the new Ta-Zr oxide initially had lower specific BET surface area than the CESI standard washcoat materials. But compared with our current washcoat material (Figure 4.3.1) they show superior surface area after aging for 1000 hours under simulated combustion conditions. This result is in agreement with previous results for high temperature calcination of Ta-Zr oxide powders in air and humid (10-vol% H₂O) air. The current result simply shows that the additional of PGM in the prepared catalyst does not change the improved stability of the new supporting oxide material.

Unfortunately the new washcoat oxide does not stabilize the active noble metal phase relative to our current washcoat material (Figure 4.3.2). After 8000-h aging under simulated combustion conditions at 900°C, the active component areas for the catalyst powder prepared using the new supporting oxide are almost the same as the catalysts prepared from the current material.

Catalyst Description	Parameter	Aging Time (h)								
		4	20	62	318	1000	2000	4000	6000	8000
CESI std powder	BET SA (m ² /gm)	22.7	21	19	12.7	8.4	7	6	5	4.4
	Exposed metal area (a.u.)	38	35	31	22	13.2	13.1	6.5	6.9	5.0
CESI std monolith	BET SA (m ² /gm)	17.4	16	14.4	10.2	6.1	5.5	4.9	4.7	4.4
	Exposed metal area (a.u.)	24	23	21	18.9	12.8	5.6	3.9	3.0	2.0
Ta-Zr oxide powder	BET SA (m ² /gm)	--	14.3	--	9.1	8.5	7.4	7.1	--	--
	Exposed metal area (a.u.)	--	14.3	--	4.0	3.1	2.2	1.6	--	--

Table 4.3.1 -- Normalized results of the analysis for total (BET) surface area and exposed metal content for the 900°C HPAR aged catalysts

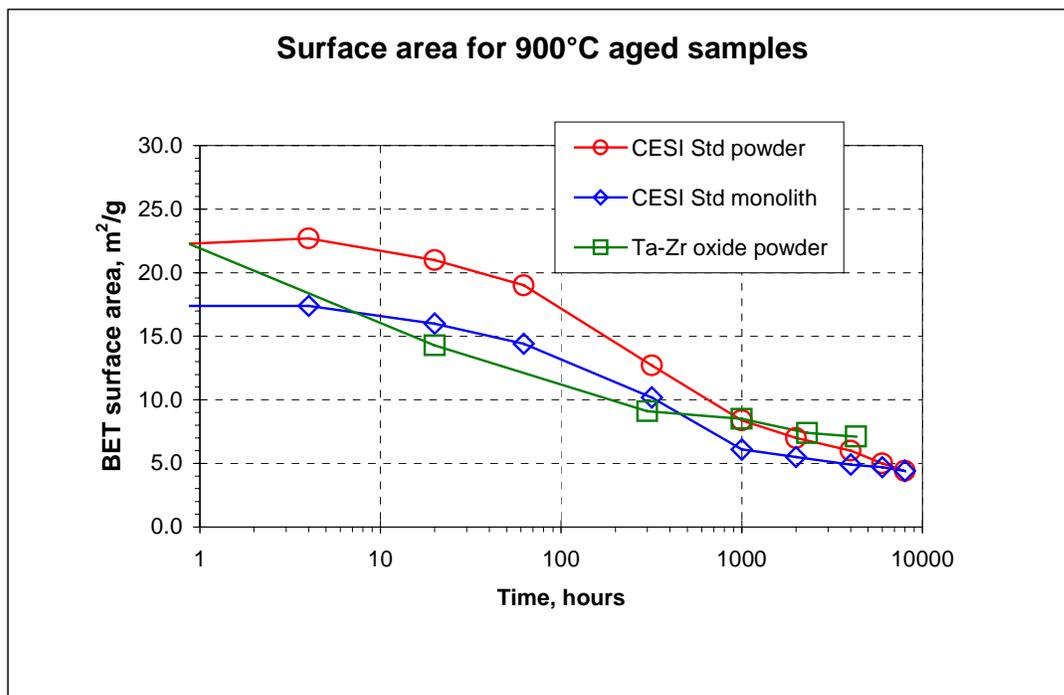


Figure 4.3.1 -- Total (BET) surface area analysis results for catalysts aged at 900°C

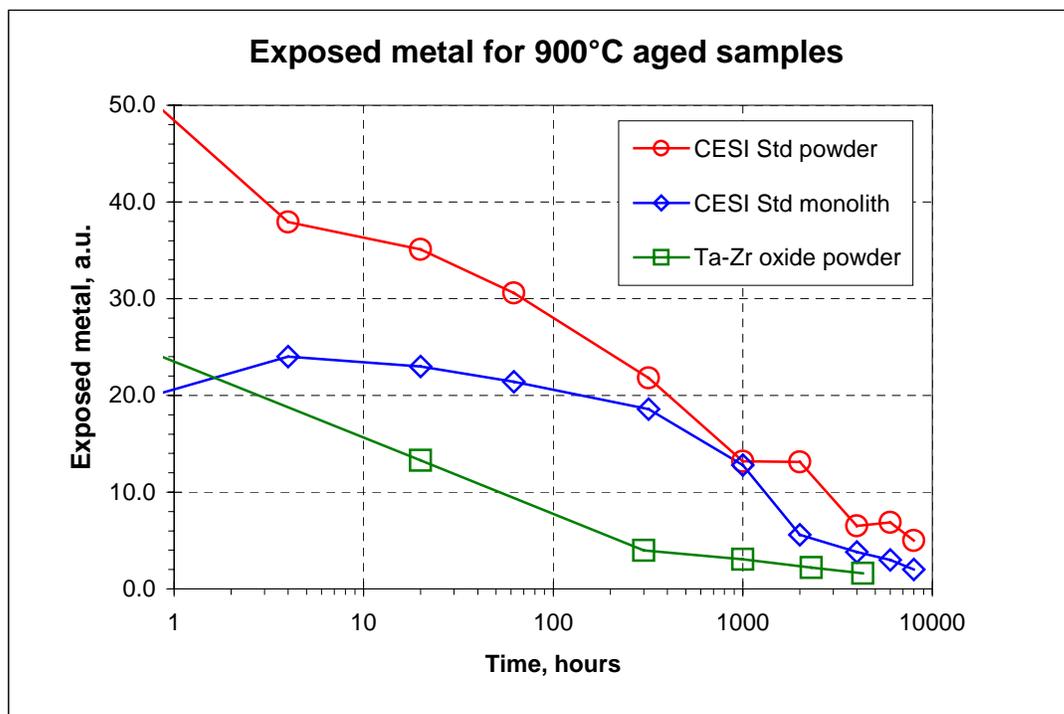


Figure 4.3.2 -- Active component surface area for catalysts aged at 900°C

975°C HPAR results

The results for the 975°C HPAR tests (Table 4.3.2) show very similar trends as the 900°C results. Catalysts prepared from the new Ta-Zr oxide washcoat again show lower specific BET surface area initially, but begin to show superior surface area after aging only 1000-h under simulated combustion conditions compared with our current washcoat material (Figure 4.3.3). Unfortunately the new washcoat supporting oxide does not stabilize the active noble metal phase relative to our current washcoat material (Figure 4.3.4). After 4000-h aging under simulated combustion conditions, the active component areas for the catalyst powder prepared using the new supporting oxide is almost the same as the catalysts prepared from the current material.

Catalyst Description	Parameter	Aging Time (h)					
		30	100	300	1000	2000	4000
CESI std powder	BET SA (m ² /gm)	19	10.1	6.4	4.2	3.2	2.3
	Exposed metal area (a.u.)	23	15.3	13.5	8.1	--	7.2
CESI std monolith	BET SA (m ² /gm)	16	14.4	10.2	6.1	5.5	4.9
	Exposed metal area (a.u.)	17.3	11.6	8.4	4.6	3.9	3.2
Ta-Zr oxide powder	BET SA (m ² /gm)	10.3	8.6	7.2	5.8	5.2	4.7
	Exposed metal area (a.u.)	9.3	7.3	8.2	4.9	3.7	3.9
Ta-Zr oxide monolith	BET SA (m ² /gm)	12.8	10.7	8.8	6.7	6.2	5.6
	Exposed metal area (a.u.)	26	10.1	5.5	4.4	3.0	3.1

Table 4.3.2 -- Normalized results of the analysis for total (BET) surface area and exposed metal content for the 975°C HPAR aged catalysts

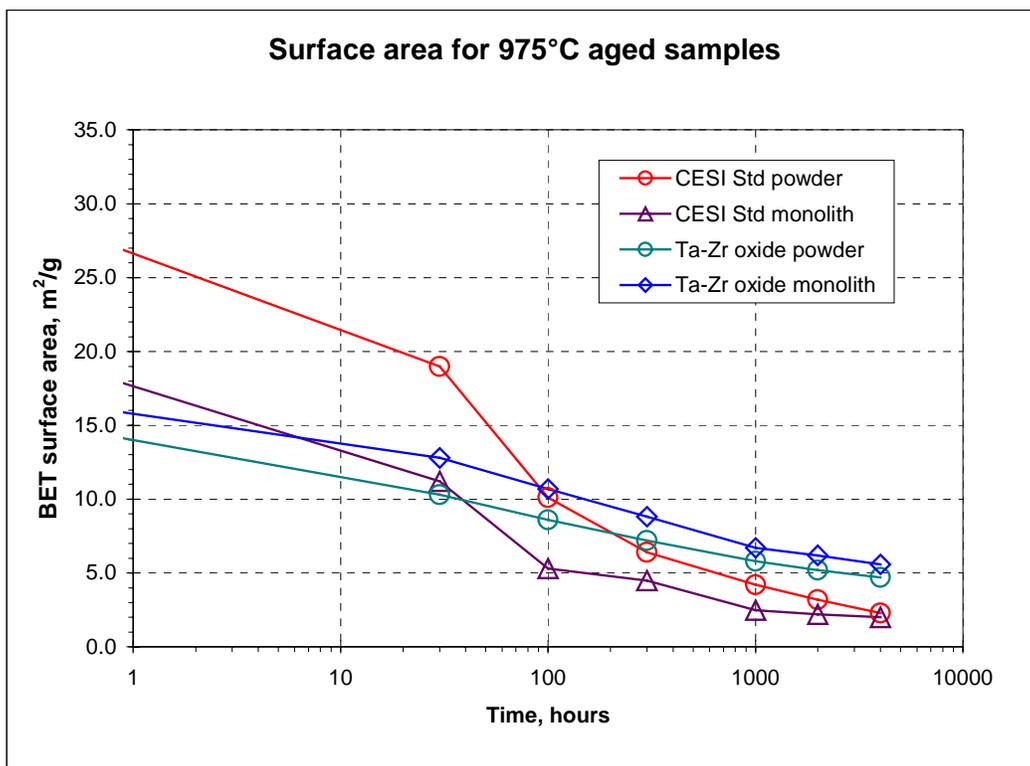


Figure 4.3.3 -- Total (BET) surface area analysis results for catalysts aged at 975°C

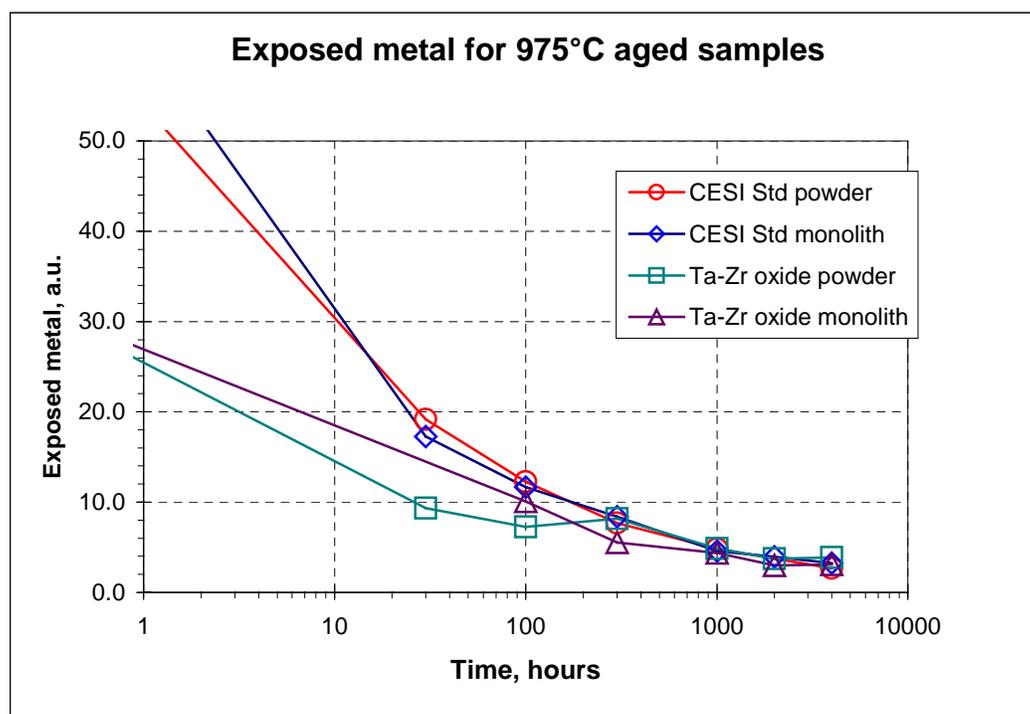


Figure 4.3.4 -- Active component surface area for catalysts aged at 975°C

V. Catalyst Performance Testing (Task 5.4)

Since the catalyst in the Xonon™ technology operates adiabatically and the flow is restricted to within small channels, the performance of a small diameter plug (e.g., 2-in.) of catalyst fully simulates the operation of the full-scale (e.g., 16-in.) system. Therefore CESI's sub-scale catalyst test facility (Figure 5.1) reproduces the conditions of pressure, temperature, gas composition, and air-flow present in a commercial gas turbine combustor. For the catalyst performance tests, a 2 inch (50mm) diameter catalyst is assembled and installed in the test section. An air compressor and the electric air heater reproduce the temperature, pressure and flow conditions representative of air entering the combustor from a gas turbine compressor. The catalyst is then tested under the cycle conditions that represent the expected operating conditions of a particular gas turbine. Catalysts prepared as described above using the new ceramic washcoat material were tested under the conditions expected in the Kawasaki M1A-13X gas turbine using the catalyst test facility. Specific work planned is as follows:

- 5.4.1. Prepare sub-scale (50-mm diameter) catalyst systems incorporating the new ceramic support materials developed in Tasks 5.1 through 5.3.
- 5.4.2. Determine catalyst performance over the gas turbine operating conditions from start up and through the load range to full load. Compare performance of the new catalysts with the performance of the current commercial catalyst.
- 5.4.3. Perform extended tests after establishing stable performance. These tests are expected to be 100 to 200 hours in duration with periodic evaluation of the catalyst "reactivity".
- 5.4.4. After completion of these tests, the catalyst systems will be characterized through surface area measurements and SEM. In particular, the surface area data will be compared with the data from the thermal aging work done in Task 5.3 at similar aging times.

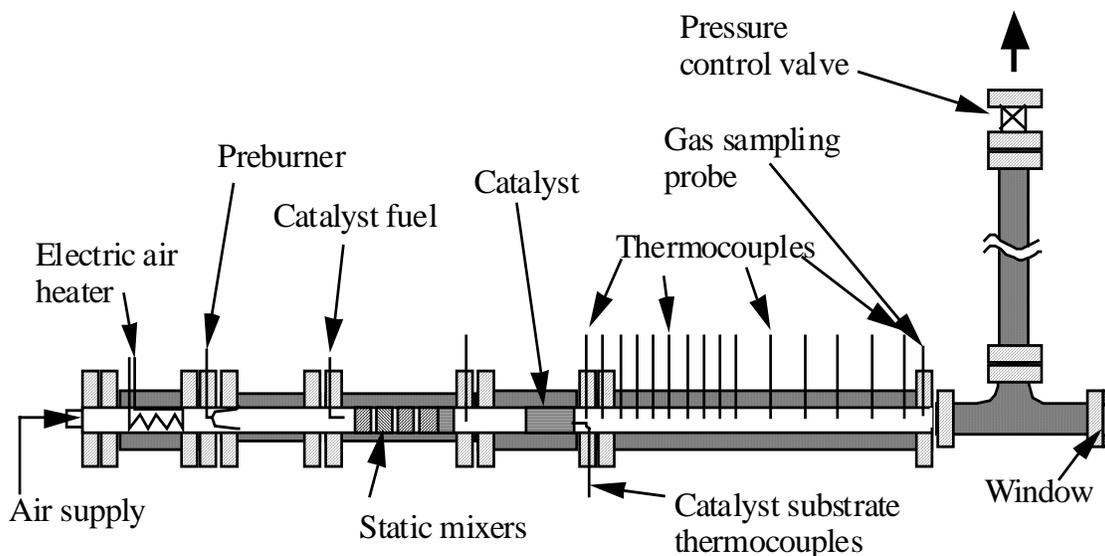


Figure 5.1 -- High-pressure sub-scale catalyst test facility

5.1 Monolith preparation procedure (Task 5.4.1)

The monolith parameters targeted for preparation were those used for the second stage of the Kawasaki M1A-13X catalyst system. The new washcoat powders were prepared and applied to the foils as described above in Section III. The final washcoat loading was 6.74 mg/cm^2 foil surface area. A standard first stage catalyst, an early design for the Kawasaki M1A-13X catalyst module, was used in series (upstream) of the new monolith for all tests. Both stages were instrumented with thermocouples, rolled to 2" diameter, and installed into the subscale test facility for investigation of performance and short-term durability.

5.2 Subscale 2-stage monolith system test results (Task 5.4.2)

Light-off tests were performed to determine initial light-off temperatures (LOT) for both stages. This test was followed by a 300-hour durability test of catalyst performance at Kawasaki M1A-13X turbine full-load conditions. Periodic light-off tests were performed to track catalyst activity as a function of reciprocal temperature versus time. Table 5.2.1 displays the conditions for each type of test. Figure 5.2.1 shows the light-off test results for the stage 2 catalytic monolith prepared using the new Ta-Zr mixed oxide material (labeled as *Ta-ZrO₂ catalyst '98*). The current system was identical to the monolith system previously tested in 1995 using sol-gel derived Ta-Zr oxide research materials as a support in stage 2 (labeled as *Ta-ZrO₂ catalyst '95*). Also included in the figure are test results for a catalyst prepared using the current commercial support (labeled as *baseline catalyst '98*) and the corresponding previous baseline catalyst (labeled as *baseline catalyst '95*). It is very clear and reproducible that the initial and short-term performance of catalyst prepared using the new Ta-Zr supporting oxides are superior to those of the commercial materials.

Inlet temperature ramp-up (light-off temperature) tests		Steady-state tests	
Air flow/SLPM	4210	Air flow/SLPM	4210
Pressure/atm	9.4	Pressure/atm	9.4
Inlet temperature (°C)	300-600	Inlet temperature (°C)	400
Tad/(°C)	1000	Tad/(°C)	1350

Table 5.2.1 -- Catalyst performance and short-term durability test conditions

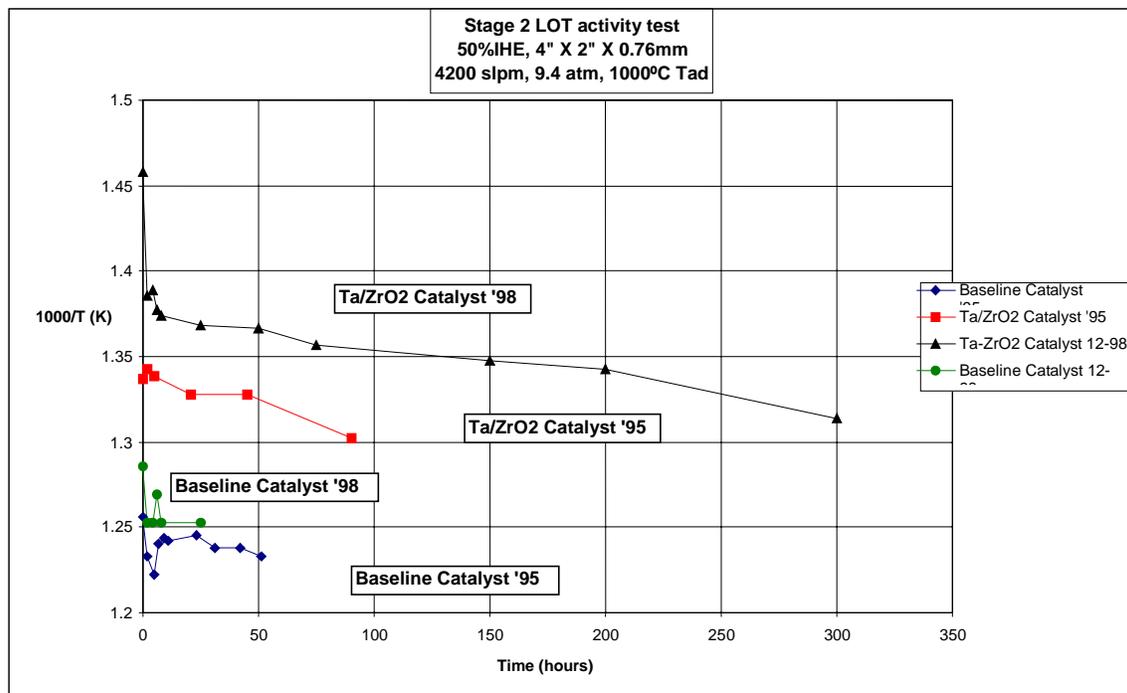


Figure 5.2.1 -- Sub-scale catalyst performance (light-off) test results

5.3 Test results for short-term durability (Task 5.4.3)

The inlet and outlet gas temperatures and the corresponding fuel conversion data for the durability test with the new Ta-Zr oxide catalyst and the corresponding baseline catalyst (Figure 5.3.1) show that the new material is more stable over a few hundred hours operation. This result is perhaps attributable to the greater initial activity of the Ta-Zr oxide supported catalyst.

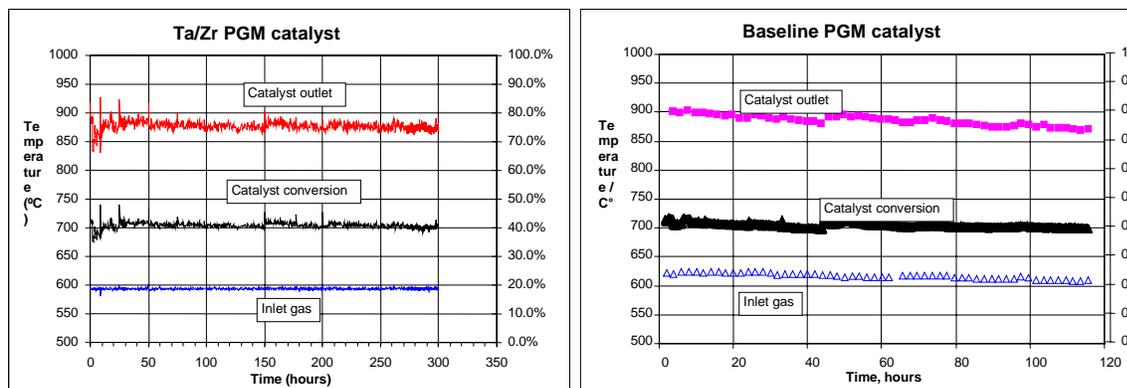


Figure 5.3.1 -- Results of sub-scale short-term durability tests

5.4 Characterization of tested catalysts

Subsequent to the durability tests, a section of the Ta-Zr oxide supported catalytic monolith foil was cut into inlet and outlet halves and scraped to remove the catalyst material. A fresh piece of monolith foil was saved before testing and scraped for comparison with the sample taken after

aging. The scraped samples were analyzed for BET total surface area via N₂ physisorption and by titration of reduced metal surface using hydrogen titration (Table 5.4.1). Included in Table 5.4.1 are results from a baseline monolith catalyst aged in the pressurized aging furnace (HPAR) at 900°C as well as the HPAR results for the new Ta-Zr oxide based catalyst as described in Section III. The physical conditions of the HPAR aging test mimic the conditions used during the sub-scale durability tests with the exception of a much lower flow rate and the absence of heat release by oxidation of the fuel. The specific surface areas of the Ta-Zr oxide supported catalyst both total and reduced metal (the active component) initially were moderately lower (~10%) than the baseline catalyst, but showed moderately superior (~10%) values after 300-h aging in sub-scale tests and in the HPAR reactor. This confirms the greater short-term stability of catalysts prepared with the new supporting oxide seen in the sub-scale tests.

Catalyst sample & reference number	BET total surface area (m ² /g)	Exposed metal content by H ₂ titration (a.u.)
Ta-Zr oxide (no metal), 1000°C/10-hrs 886-149-1	26.4	-
Ta-Zr oxide catalyst fresh 1020-021-B	16.3	30.0
Ta-Zr oxide catalyst aged inlet half 1020-021-IB300	13.6	25.6
Ta-Zr oxide catalyst aged outlet half 1020-021-OB300	12.5	27.8
Baseline catalyst fresh 886-141-D	17.4	37.0
Baseline catalyst HPAR aged 300-hrs 886-141-D300	10.2	23.0

Table 5.4.1 -- Characterization of fresh and aged catalysts

VI. Improved Catalyst System Demonstrated (Task 5.5)

The data from Task 5.3 and 5.4 allowed us to assess the level of improved performance from the new catalyst materials. The sub-scale tests (Task 5.4) through 300-h showed the superior initial performance and the superior short-term stability of the new materials. The 8000-h stability of the total surface area (Task 5.3) in the presence of the metal and under commercially relevant conditions was also encouraging. These promising results were encouraging, but not sufficient to show a milestone improvement. The long-term performance of the catalyst, based on the stability of the active metal surface dispersed by new supporting oxide, was found not to be superior to that of the commercial baseline catalyst after 8000-hours at 900°C and 4000-hours at 950°C. The stability of the supporting oxide apparently is not sufficient to prevent the loss of surface area of the active metal.

VII. Production of Engine Catalyst (Task 5.6)

The work in this task includes:

- 5.6.1. Prepare a full-scale catalyst module for Kawasaki M1A-13X in-engine tests.

5.6.2. Incorporate the new catalyst into the RAMD Pier 1 program.

Based on the long-term performance as assessed in Tasks 5.3 and 5.5, a full engine catalyst was not warranted. This catalyst system was not incorporated into the RAMD testing program of Task 1.

VIII. Summary of Task 5 Accomplishments

The primary objective of Task 5 was to prepare and test the short- and long-term performance of thermally stable catalysts using commercially scaleable processing and commercially relevant test conditions. This objective was fully accomplished, but the long-term stability of the catalytically active metal component proved to be comparable to the current catalytic material.

Specific accomplishments are listed below:

- After a preliminary evaluation of co-precipitation processing, the most important steps in the preparation of mixed Ta-Zr oxide powders were identified as mixing and drying.
- Precipitation of the Ta-Zr mixed oxide was found to be a viable and more commercially attractive process than sol gel methods. The use of a dual chamber sonic jet mixer combined with commercial batch CO₂ supercritical drying of centrifuged precipitates produced materials equivalent to those prepared using sol-gel approaches.
- Catalytic monolith tests using the precipitated powders verified earlier results which showed that catalytic monoliths prepared using Ta-Zr mixed oxide as a support exhibit superior light-off performance even after 300 hours of sub-scale testing under conditions simulating turbine combustion under full load conditions.
- Catalysts prepared with the new Ta-Zr oxide showed greater short-term (300-h) stability for the active metal surface area than the current formulation. The activity of the catalysts prepared with the new oxide was about twice that of those prepared current baseline supporting oxide when normalized by reduced metal surface area measurements. An investigation into the enhancement of specific combustion activity by the Ta-Zr oxide supported catalyst is an interesting finding, but it was not investigated further.
- Unfortunately the stability of the active metal surface area was not sustained for 8000-hours at 900°C and 4000-hours at 950°C. Therefore, full-scale testing with the new more expensive supporting oxide material was not justified.

Since the completion of this task, subsequent investigations of the long-term aging of supported metal catalyst have also shown that the stability of the ceramic dispersing oxide is not sufficient to insure stability of the active metal component.