COUPLING OF TRANSPORT AND CHEMICAL PROCESSES
IN CATALYTIC COMBUSTION

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Catalytic combustors have demonstrated the ability to operate effi-
ciently over a much wider range of fuel air ratios than are imposed by the
flammability limits of conventional combustors. Extensive commercial use
however awaits further progress in the areas of i) the design of a catalyst
with low ignition temperature and high temperature stability, ii) reducing
fatigue due to thermal stresses during transient operation and, iii) the
development of mathematical models that can be used as design optimization
tools to isolate promising operating ranges for the numerous operating
parameters.

The catalytic combustion program at Princeton reflects these needs for
further research. The current program of research involves the development
of a two-dimensional transient catalytic combustion model and the develop-
ment of a new catalyst with low temperature light-off and high temperature
stability characteristics.

A recently developed two-dimensional transient model has been
used to study the ignition of CO/Air mixtures in a platinum coated cataly-
tic honeycomb. This model includes coupling between the gas and substrate,
radiative heat loss to the outside and radial heat losses providing solu-
tions for the two-dimensional temperature field in the substrate and the
two-dimensional temperature, composition and velocity field in the gas.
The model has been used to predict the transient and steady state using
inlet conditions for which steady state experimental data is available. In
the calculation the inlet conditions for velocity and temperature are set
and the transient begins by injecting fuel. Results showing the transient
behavior of the substrate and the gas are presented. This model is par-
ticularly useful for predicting the temperature gradients in the substrate
which in turn can be used to predict the thermal stresses in the catalyst

during the transient. Since transient measurements are not available the calculated steady state results are compared to steady state measurements. The predicted steady state catalyst temperature profile and the exhaust gas composition are found to agree very well with measurements over a range of inlet velocities and equivalence ratios.

Operating temperatures of catalytic combustors often exceed 1500 K, resulting in unacceptably short lifetimes for standard catalysts. A new catalyst has been designed to exhibit long lifetime at high temperatures and adequate ignition characteristics at low temperatures. The catalyst is a modified perovskite based on La $(Cr_{0.5} Al_{0.5}) O_3$. This ceramic has been doped to make it electrically conductive and consequently it can be resistively heated to bring the catalyst up to the required light-off temperature. In addition, platinum has been incorporated into the crystal structure to give improved low temperature light-off while having a low platinum vapor pressure at high operating temperatures. This catalyst can be used in powdered form, by washcoating it onto a high temperature ceramic substrate, or as sintered monolythic structures, e.g. plates. The advantage of using the catalyst in the form of plates is that they can be resistively heated to assist light-off. However, the catalyst is more readily available in powdered form and therefore the first tests with the new catalyst have been made with it washcoated on a honeycomb substrate. The substrate used was mullite, three inches long with 1/16 inch square cells. Results of experiments using a pure platinum washcoat and a perovskite powder with nominal 1.0% (by weight) platinum washcoat are presented. The tests consist of establishing the light-off temperature and low temperature performance for several equivalence ratios and inlet velocities, after which the catalyst is "aged" for several hours at 1500 °K and then the light-off and low temperature experiments repeated. Preliminary results are very encouraging indicating very little change in surface activity when used with propane fuel. Tests with hydrogen however indicate a poisoning effect which quickly reduces the activity of the catalyst. Results from these tests will be used as a guide in the selection of the optimum platinum content, in terms of both adequate low temperature light-off and minimal high temperature aging, to be used in the catalytic plates which will be produced and tested in the near future.

TRANSIENT CATALYTIC COMBUSTION MODEL

- SOLVES COMPLETE COUPLED 2-D TRANSIENT CONSERVATION EQUATIONS IN BOTH SOLID AND GAS

- PREDICTS TRANSIENT AND STEADY STATE, 2-D TEMPERATURE IN SUBSTRATE, 2-D VELOCITY/COMPOSITION/TEMPERATURE IN GAS

- INCLUDES RADIATION WITHIN CATALYST BED AND FROM FRONT/BACK TO UP/DOWN STREAM COMBUSTOR WALLS

- INCLUDES RADIAL HEAT LOSSES (I.E. NON-ADIABATIC)

- HAS BEEN USED TO PREDICT TRANSIENT AND STEADY STATE CO/AIR CATALYTIC COMBUSTION IN PLATINUM COATED HONEYCOMB CATALYSTS USING ONE STEP OVERALL REACTION FOR GAS AND WALL REACTIONS
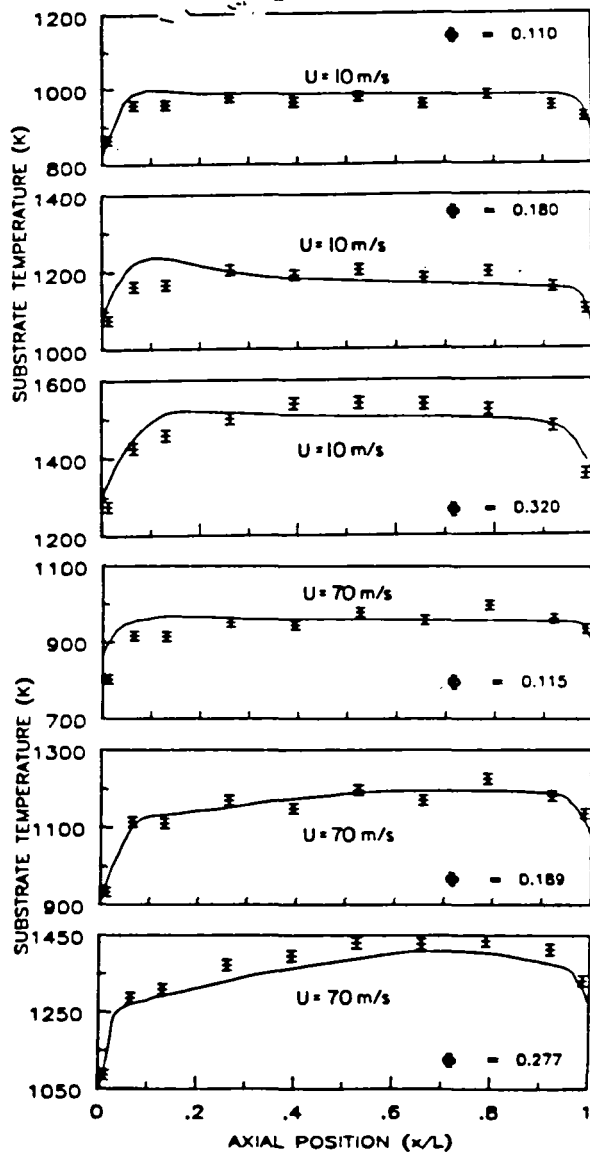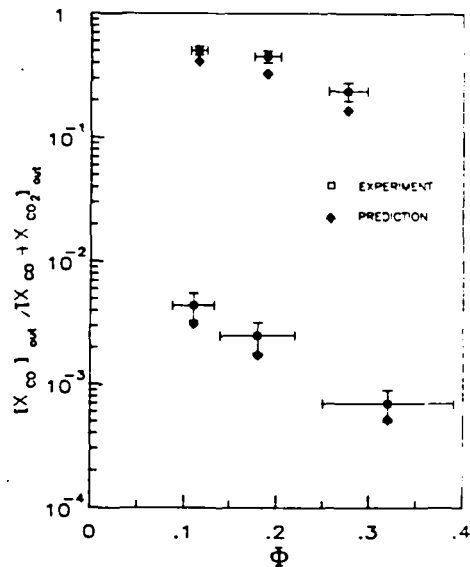
INLET CONDITIONS FOR TRANSIENT CALCULATION

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VELOCITY	10 M/SEC
TEMPERATURE	600 K
PRESSURE	110 KPA
FUEL	CARBON MONOXIDE
EQUIVALENCE RATIO	0.32
ADIABATIC FLAME TEMPERATURE	1580 K
WATER MOLE FRACTION	5.4×10^{-5}
MACH NUMBER	0.02
REYNOLD'S NUMBER	290
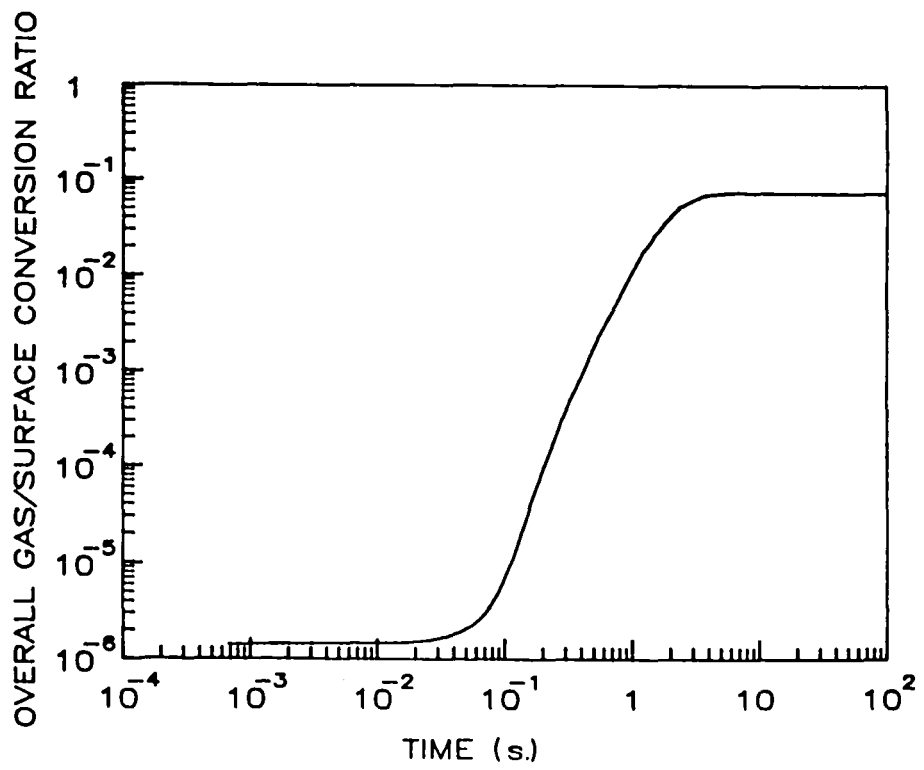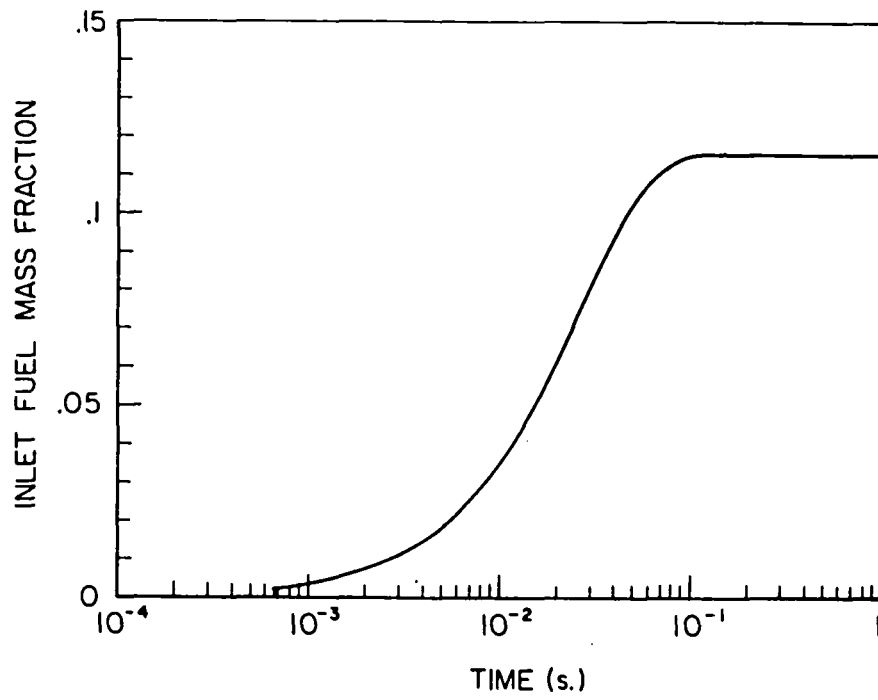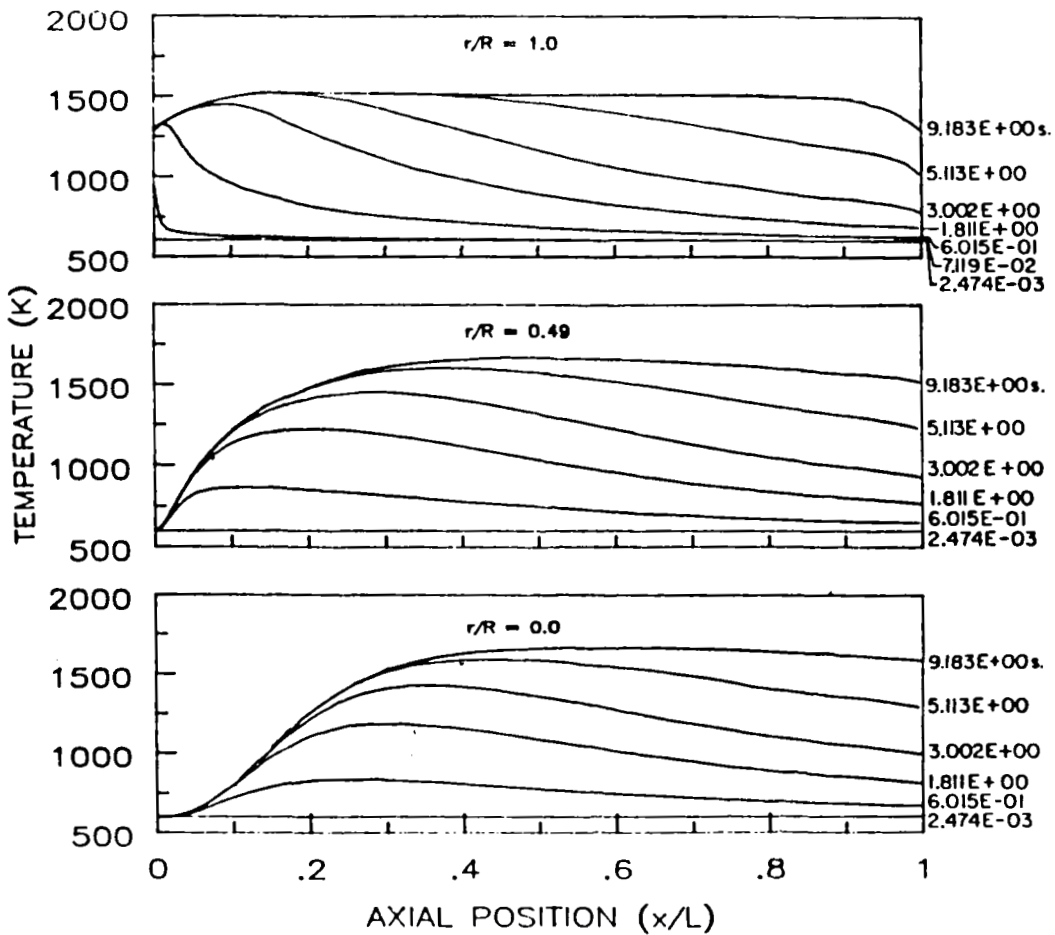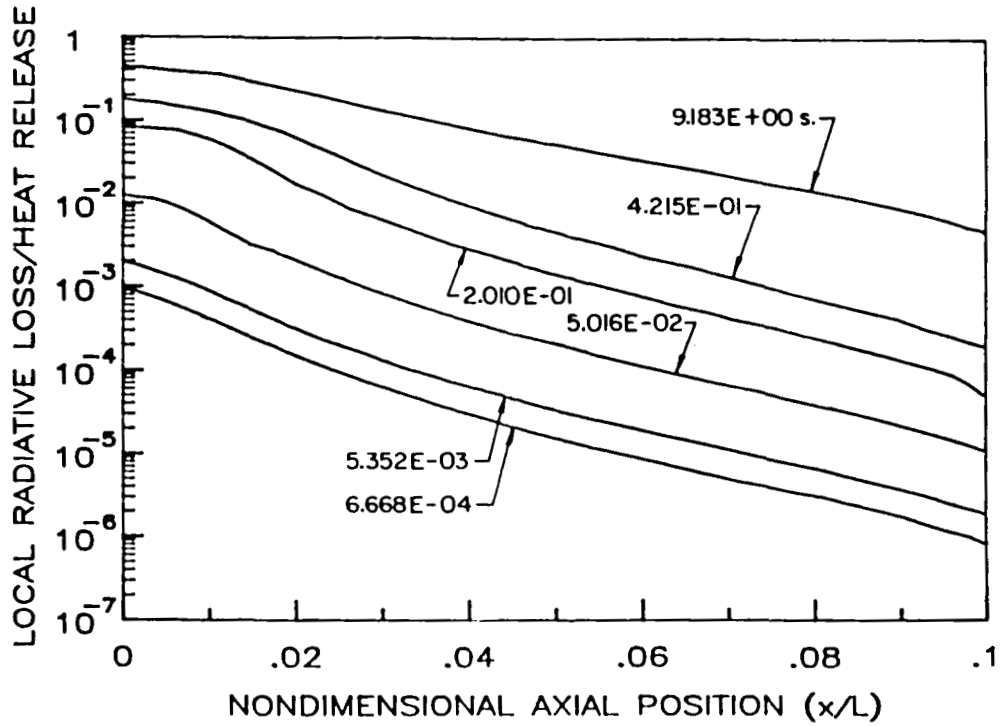
* THE INITIAL HEAT RELEASE OCCURS NEAR THE ENTRANCE AT THE
  GAS-SOLID INTERFACE AND IS CONTROLLED BY HETEROGENEOUS
  REACTIONS.

* LARGE SPATIAL AND TEMPERAL TEMPERATURE GRADIENTS OCCUR IN
  THE SOLID NEAR THE ENTRANCE CONTROLLED MOSTLY BY THE
  AVAILABILITY OF FUEL.

* THE TEMPERATURE OF THE SOLID NEAR THE ENTRANCE ACHIEVES ALMOST
  ITS FINAL VALUE BEFORE SIGNIFICANT HEATING OF THE BACK.

* HETEROGENEOUS REACTIONS AND THE GAS HEATED UP FRONT AND FLOWING
  DOWNSTREAM HEAT THE BACK OF THE SOLID.

* THE OVERALL TRANSIENT TIME IS CONTROLLED BY THE THERMAL INERTIA
  OF THE SOLID AND BY FORCED CONVECTION.

* RADIATION SIGNIFICANTLY INFLUENCES BOTH TRANSIENT AND STEADY
  STATE PARTICULARLY NEAR THE ENTRANCE.

* THE OXIDATION OF CO OCCURS MOSTLY ON THE CATALYST AND SOON INTO
  THE TRANSIENT BECOMES DIFFUSION CONTROLLED.

Graph axes: y-axis $[X_{CO}]_{out}/[X_{CO} + X_{CO_2}]_{out}$ with values 1, 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}; x-axis Φ with values 0, $.1$, $.2$, $.3$, $.4$. Legend: □ EXPERIMENT, ◆ PREDICTION

DEVELOPMENT OF NEW CATALYST FOR HIGH TEMP OPERATION

I) Two Objectives

   A) Low Temperature Light-Off; Pt in Crystal Structure

   B) High Temperature Stability, Particularly Against Loss of Pt

II) Perovskites, ABO$_3$, Chosen as Class of Material to be Employed
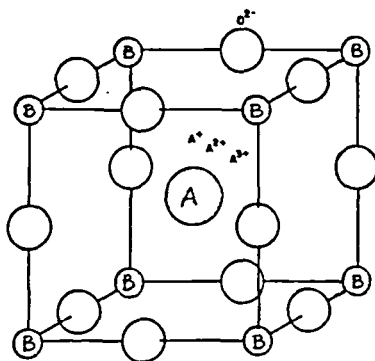
CRYSTAL STRUCTURE

Approximately Cubic

Easy Substitution of Impurities

At A and B Sites

To Control Properties

1) Perovskites have been evaluated as MHD materials, and have proven high temperature endurance and catalytic activity

2) The material is electrically conductive and may be heated by applied voltage, enabling precise light-off control

3) Platinum dopant added for low temp. light-off capability; the Pt is chemically bound in the crystal structure for stability and endurance

4) Monolythic design overcomes drawbacks of inert substrate + active coating catalysts

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III) COMPOSITIONS OF MATERIALS FABRICATED

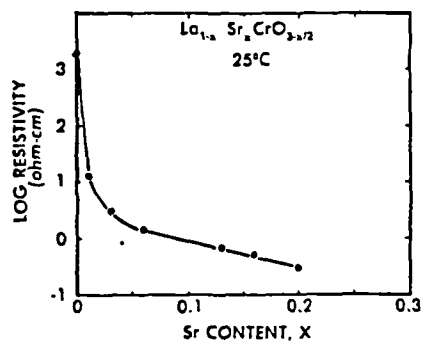A) $(La_{0.95}\ Sr_{0.05})[Cr_{0.499}\ Al_{0.5}\ Pt_{0.001}]\ O_3$

MADE BY TRANSTECH AND SUPPIED BOTH AS A POWDER FOR SLIP COATING AND AS MONOLYTHIC PLATES AND SPACERS FOR PARALLEL PLATE REACTOR

B) $La\ [Mg_{0.05}\ Cr_{0.47}\ Al_{0.47}\ Pt_{0.01}]\ O_3$

MADE BY PROF. HARLAN ANDERSON, UNIVERSITY OF MISSOURI, AND SUPPLIED AS A POWDER SUITABLE FOR SLIP COATING
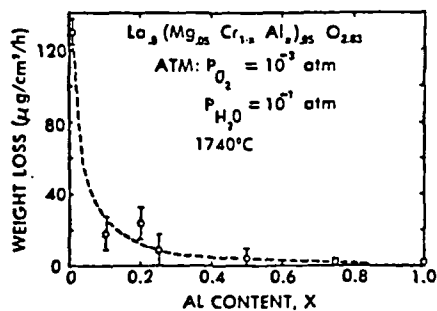
IV) BASIS FOR THESE CHOICES

A) ELECTRICAL CONDUCTIVITY

DATA FROM
MEADOWCROFT, D.B.
BRIT. J. APP. PHYS 2
(1969) 1225

B) HIGH TEMPERATURE STABILITY

DATA FROM
PROF. H.O. ANDERSON

Weight loss (Mg/cm^2/h) of La$_{.9}$(Mg$_{.05}$Cr$_{1-x}$Al)$_{.95}$O$_{2.85}$ as function of Al content: Temperature = 1740°C; Atm: Flowing gas mixture (0.001 atm O$_2$+0.1 atm H$_2$O+N$_2$); Flow rate = 1

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v) TEST CONFIGURATIONS

A) SLIP COATED ONTO A SUBSTRATE. AL_2O_3 IS A PREFERRED SUBSTRATE FOR HIGH TEMPERATURE OPERATION. FOR LIGHT-OFF TESTS, MULLITE MAY BE USED.

DISADVANTAGES PHASE DIAGRAM PROBLEMS; NO DIRECT ELECTRICAL HEATING FOR LIGHT-OFF CONTROL.

ADVANTAGES PERMITS RAPID TEST OF MATERIAL UNDER COMBUSTION CONDITIONS

B) MONOLYTHIC STRUCTURES - POWDERS MAY BE SINTERED TO PRODUCE MONOLYTHIC MATERIALS IN THE FORM OF PLATES. DENSITIES BETWEEN 75% AND 95% THEORETICAL ARE ACHIEVABLE AND PROVIDE ADEQUATE PLATE STRENGTH.
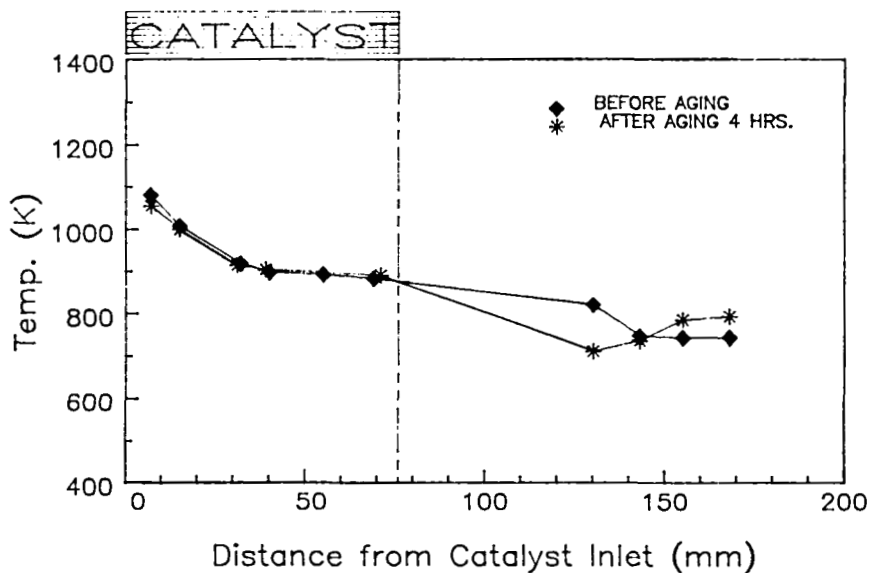
DISADVANTAGES THERMAL SHOCK CRACKING OF MONOLYTHS (NEED TO CONTROL DENSITY AND COMPOSITION TO MINIMIZE THIS.)
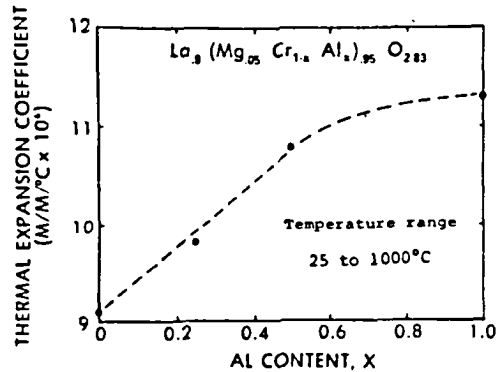

ADVANTAGES ELECTRICAL HEATING POSSIBLE FOR REACTION INITIATION. GOOD EXPERIMENTAL ACCESS, ESPECIALLY FOR LASER PROBES.
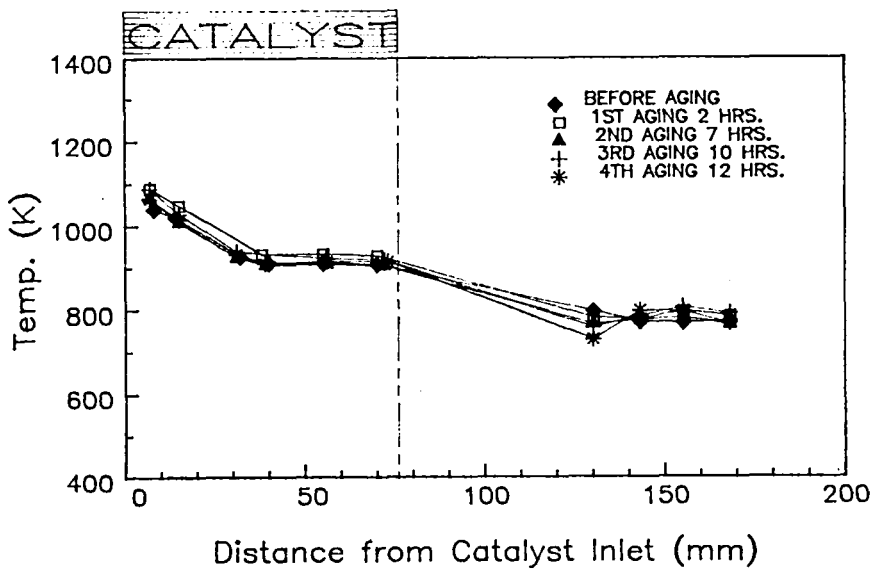
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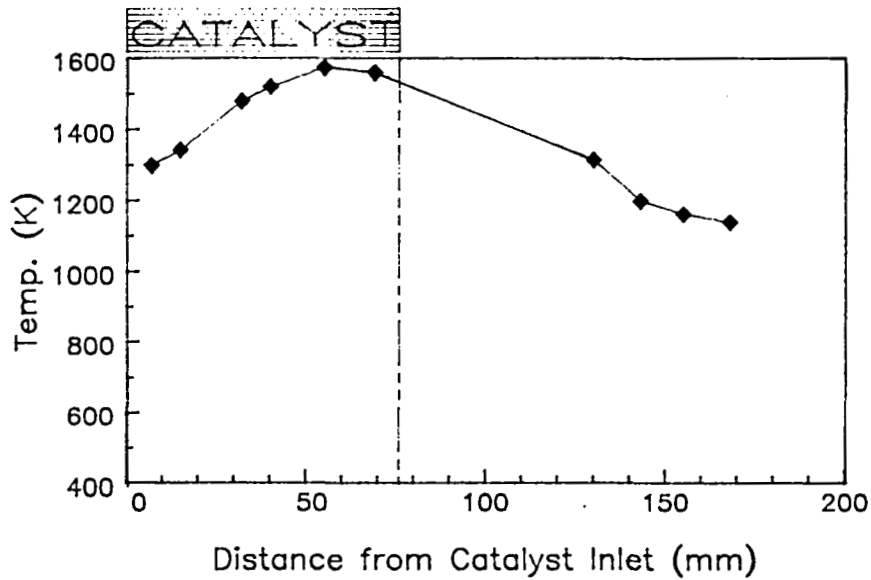
AGING OF PURE PLATINUM CATALYST
PROPANE FUEL, EQUIVALENCE RATIO = 0.42
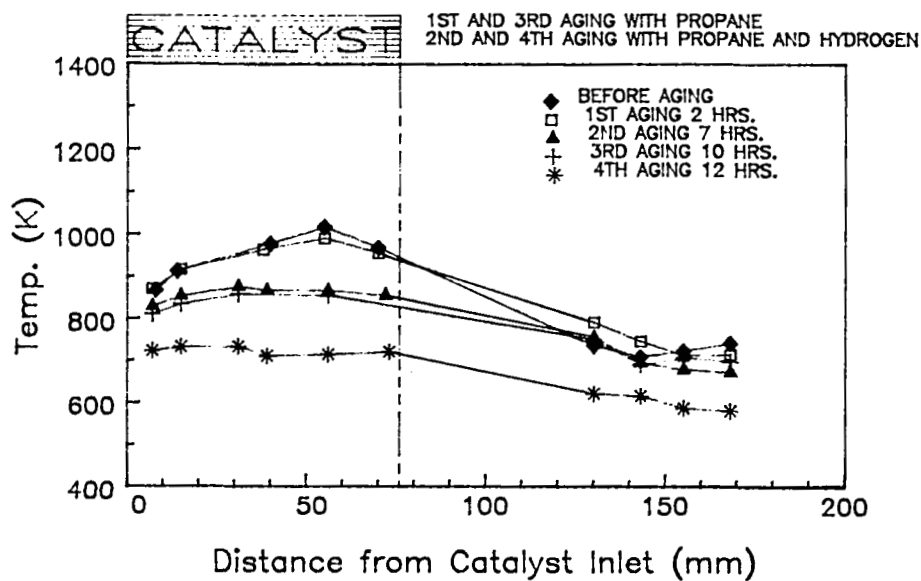INLET TEMP. = 688 K, INLET VELOCITY = 9.9 m/s

PURE PLATINUM CATALYST
HYDROGEN FUEL, EQUIVALENCE RATIO = 0.1
INLET TEMP. = 590 K, INLET VELOCITY = 10.2 m/s

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CATALYST

Temp. (K) vs Distance from Catalyst Inlet (mm)

BEFORE AGING
AFTER AGING 4 HRS.
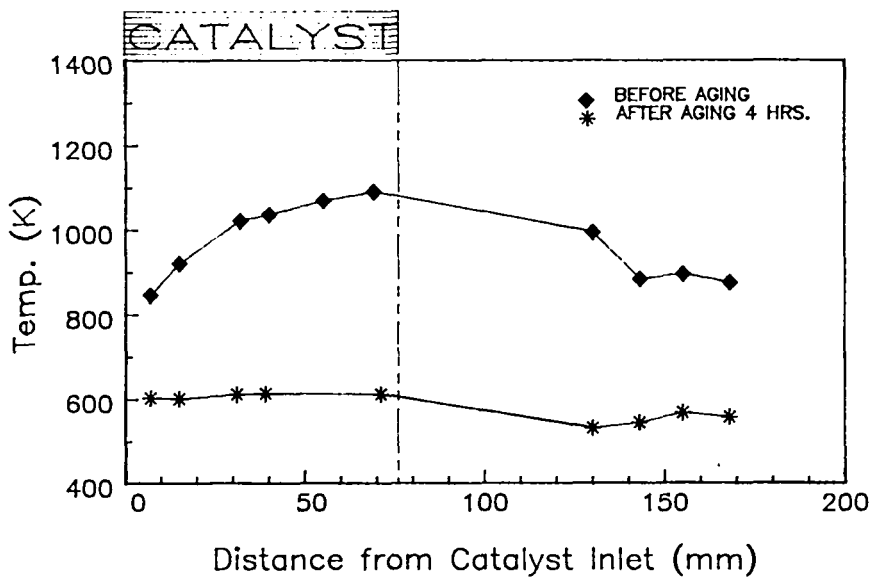
PURE PLATINUM CATALYST
PROPANE FUEL, EQUIVALENCE RATIO = 0.28
INLET TEMP. = 589 K, INLET VELOCITY = 10.1 m/s

CATALYST

Temp. (K) vs Distance from Catalyst Inlet (mm)

BEFORE AGING
1ST AGING 2 HRS.
2ND AGING 7 HRS.
3RD AGING 10 HRS.
4TH AGING 12 HRS.

PEROVSKITE WITH NOMINAL 1% BY WEIGHT
PLATINUM CATALYST
HYDROGEN FUEL, EQUIVALENCE RATIO = 0.10
INLET TEMP. = 591 K, INLET VELOCITY = 10.1 m/s

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PEROVSKITE WITH NOMINAL 1% BY WEIGHT
PLATINUM CATALYST
PROPANE FUEL, EQUIVALENCE RATIO = 0.30
INLET TEMP. = 698 K, INLET VELOCITY = 6.0 m/s