Operation Regimes in Catalytic Combustion: H_2/Air Mixtures near Pt

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The influence of a platinum catalyst on flammability limits and operation windows for catalytic and catalyst-assisted homogeneous oxidation is studied, for the first time to our knowledge, as a function of H_2 in air composition in a stagnation-point flow geometry. The results show that the coupling between the homogeneous and heterogeneous chemistries leads to relatively easy startup, the coexistence of catalytically (partially) and homogeneously (completely) ignited branches under certain conditions, and the expansion of the fuel-lean and rich flammability limits. A strategy to attain virtually any desired operation regime is discussed. It is shown that synergism between homogeneous and heterogeneous chemistries leads to higher combustion efficiency and lower fuel emissions at elevated temperatures for fuel-lean mixtures only. Analysis of the flammability limits indicates that heat generated by surface reactions is primarily responsible for expansion of the flammability limits. Finally, a direct transition to flames occurs over a wide range of composition upon catalytic ignition in the absence of surface heat loss.

Introduction

Although homogeneous combustion has traditionally been the primary method for oxidizing fuels, catalytic oxidation is known to have several advantages over homogeneous combustion alone. For example, it has been shown that a catalytic surface can stabilize a flame, facilitate reactor startup, reduce pollutant emissions such as unburned fuel and NO_x, and enable self-sustained combustion beyond the homogeneous flammability limits (Prasad et al., 1984; Pfefferle and Pfefferle, 1986, 1987). In addition, while homogeneous oxidation is usually of interest only for energy production, catalytic oxidation is also a major method for producing valuable chemicals via so-called partial or selective oxidation (Satterfield, 1991). As environmental regulations become more stringent, further research and innovations in catalytic combustion can be expected.

At present, catalytic oxidation of many systems is not well understood, due to complex interactions between the homogeneous and heterogeneous reactions. An exception to this generalization is the oxidative coupling of methane (Bistolfi et al., 1992). Some of the previous modeling efforts have used global or simplified surface kinetics to describe catalytic combustion (Song et al., 1990, 1991; Markatou et al., 1991, 1993). However, this approach can be inadequate under certain conditions (Vlachos and Bui, 1996). Recent work on modeling catalytic ignition with detailed gas and surface chemistries is worth mentioning (Deutschmann et al., 1996; Rinnemo et al., 1997). In an effort to develop reliable predictive models for catalytic combustion, we have recently initiated a research program to study issues such as catalytic ignition (Vlachos and Bui, 1996; Bui et al., 1997a,b) and homogeneous ignition in the presence of a catalyst (Bui et al., 1996; Vlachos, 1996a), using detailed homogeneous and heterogeneous kinetics, and simplified multicomponent transport.

Despite previous studies, the role of homogeneous–heterogeneous interactions in reactor operation regimes and safety has not yet been addressed. For example, whether the catalyst acts purely as a flame holder upon homogeneous ignition or assists homogeneous combustion in pollutant reduction is not clear (Pfefferle and Pfefferle, 1987). From an engineering point of view, such modeling results can be valuable and could guide future experiments. Hence, in this article, we address, for the first time, the role of a platinum catalyst in operation regimes for H_2/air mixtures near a stagnation surface, using detailed modeling and bifurcation theory. Results are analyzed through reaction path analysis and numerical experiments.

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Model

The reactor model is a stagnation-point flow geometry (shown in the inset of Figure 1), where a premixed H_2/air stream impinges on a flat platinum surface of infinite diameter and zero thickness. Since the inherently two-dimensional governing equations can be reduced to a one-dimensional problem (through a similarity transformation), this model offers a computationally tractable method of studying complex flame–catalyst interactions. These interactions, and specifically the surface–flame synergism, can be of direct interest in catalytic gas turbines and burners and of fundamental understanding for more complex reactors such as fluidized bed combustors. The transformed steady-state conservation equations for species, energy, and stream function are discretized along the axial centerline using a finite difference method, and solved using Newton's technique. A robust, dynamically adaptive, multiple-weight arc-length continuation algorithm has been implemented to track stationary solutions around turning points (Bui et al., 1997b). A more detailed discussion of the governing equations and the solution algorithms can be found in (Vlachos, 1996b; Bui et al., 1997b).

The 20 reversible reactions/9 species homogeneous H_2 oxidation chemistry of Miller-Bowman (1989) (Table 1) and the 13 reactions/5 species surface reaction mechanism of H_2/O_2 on Pt by Williams et al. (1992) (Table 2) are used to compute the reaction rates. The transport properties, reaction equilibrium constants, and the thermodynamic properties of reacting mixtures are calculated using the CHEMKIN formalism (Kee et al., 1990, 1991). Comparison of simulation results to both experimental homogeneous (Bui et al., 1996; Vlachos et al., 1997) and catalytic ignition (Vlachos and Bui, 1996; Bui et al., 1997a) data has shown reasonable agreement. Recent experiments on catalytic autotherms, with realistic heat losses, are also in quantitative agreement with simulations (Fernandes et al., 1998).

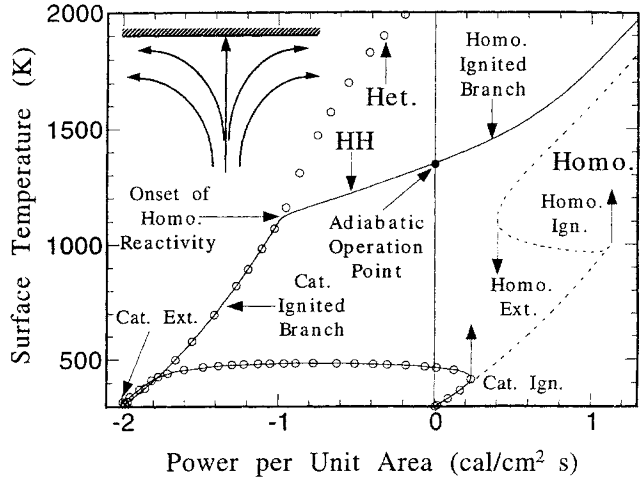

Figure 1. Surface temperature as function of power per unit area supplied to catalytic surface.

For the homogeneous only case (dotted line), the heterogeneous only case (circles), and the coupled (HH) case (solid line). At low temperatures the HH system behaves catalytically, whereas at high temperatures, it behaves mainly homogeneously. The inset shows a schematic of the stagnation geometry. The conditions are 5% H_2 in air, 1 atm, and 500 s^{-1} strain rate.

For all the results presented, the simulations have been carried out with the power input to the catalyst foil per unit area as the primary continuation parameter. Although the model generates solutions along the entire axis of symmetry, most of the results presented below (unless otherwise speci-

Table 1. 20 Reversible Reactions/9 Species Homogeneous H_2 Oxidation Chemistry of Miller and Bowman (1989)

Reaction No.	Reaction	k_o	β	E_a
1	$H_2 + O_2 \leftrightarrow 2OH$	1.700E+13	0.000	47,780
2	$OH + H_2 \leftrightarrow H_2O + H$	1.170E+09	1.300	3,626
3	$OH + O \leftrightarrow O_2 + H$	4.000E+14	−0.500	0
4	$O + H_2 \leftrightarrow OH + H$	5.060E+04	2.670	6,290
5	$H + O_2 + M \leftrightarrow HO_2 + M$	3.610E+17	−0.720	0
	Efficiencies: H_2 2.86, H_2O 18.6, N_2 1.26			
6	$HO_2 + OH \leftrightarrow H_2O + O_2$	7.500E+12	0.000	0
7	$HO_2 + H \leftrightarrow 2OH$	1.400E+14	0.000	1,073
8	$HO_2 + O \leftrightarrow OH + O_2$	1.400E+13	0.000	1,073
9	$2OH \leftrightarrow H_2O + O$	6.000E+08	1.300	0
10	$2H + M \leftrightarrow H_2 + M$	1.000E+18	−1.000	0
	Efficiencies: H_2 0.00, H_2O 0.00			
11	$2H + M \leftrightarrow H_2 + M$	9.200E+16	−0.600	0
	Efficiencies: H_2 1.00, all other species equal to 0.000			
12	$2H + M \leftrightarrow H_2 + M$	6.000E+19	−1.250	0
	Efficiencies: H_2O 1.00, all other species equal to 0.00			
13	$H + OH + M \leftrightarrow H_2O + M$	1.600E+22	−2.000	0
	Efficiencies: H_2O 5.00			
14	$H + O + M \leftrightarrow OH + M$	6.200E+16	−0.600	0
	Efficiencies: H_2O 5.00			
15	$2O + M \leftrightarrow O_2 + M$	1.890E+13	0.000	−1,788
16	$HO_2 + H \leftrightarrow H_2 + O_2$	1.250E+13	0.000	0
17	$2HO_2 \leftrightarrow H_2O_2 + O_2$	2.000E+12	0.000	0
18	$H_2O_2 + M \leftrightarrow 2OH + M$	1.300E+17	0.000	45,500
19	$H_2O_2 + H \leftrightarrow HO_2 + H_2$	1.600E+12	0.000	3,800
20	$H_2O_2 + OH \leftrightarrow H_2O + HO_2$	1.000E+13	0.000	1,800

k_o is the pre-exponential in $(cm^3/mol)^{n-1} \cdot s^{-1}$, where n is the reaction order, β is the temperature exponent, and E_a is the activation energy in (cal/mol). Third body collision efficiencies are 1, except for species explicitly stated otherwise in the reaction.

Table 2. 13 Reactions/5 Species H_2/O_2 on Pt Surface Reaction Mechanism (Williams et al., 1992)

Reaction No.	Reaction	k_0	E_a	$\Delta H_{r\times n}$
1	$H^* + O^* \rightarrow OH^* + *$	1.000E+15	2,500	−2,500
2	$OH^* + * \rightarrow H^* + O^*$	1.000E+08	5,000	2,500
3	$H^* + OH^* \rightarrow H_2O^* + *$	9.000E+16	15,000	−22,000
4	$H_2O^* + * \rightarrow H^* + OH^*$	1.800E+13	37,000	22,000
5	$2OH^* \rightarrow H_2O^* + O^*$	1.000E+15	12,300	−19,500
6	$H_2O^* + O^* \rightarrow 2OH^*$	0.000E+00	31,800	19,500
7	$H_2 + 2^* \rightarrow 2H^*$	1.000E+00	0	−18,000
8	$2H^* \rightarrow H_2 + 2^*$	1.000E+13	18,000	18,000
9	$O_2 + 2^* \rightarrow 2O^*$	2.790E−02	0	−52,000
10	$2O^* \rightarrow O_2 + 2^*$	1.000E+13	52,000	52,000
11	$H_2O + * \rightarrow H_2O^*$	0.100E+00	0	−10,800
12	$H_2O^* \rightarrow H_2O + *$	1.000E+13	10,800	10,800
13	$OH^* \rightarrow OH + *$	1.500E+13	48,000	48,000

k_o is the sticking coefficient for adsorption or the reaction preexponential in $(\mathrm{cm^2/mol})^{n-1} \cdot (\mathrm{sites/cm^2})^{-1}$ (sites/mol)$\cdot s^{-1}$ where n is the reaction order, E_a is the activation energy in (cal/mol), and $\Delta H_{r\times n}$ is the heat of reaction in (cal/mol).

fied) show the solution just above the surface, which we have found to be indicative of the behavior of the entire system.

Homogeneous–Heterogeneous Chemistry Interactions

Fuel-lean mixtures

Figure 1 shows one-parameter continuation results of the surface temperature vs. the power per unit area, for a fuel-lean mixture of 5% H_2 in air, atmospheric pressure, and 500 s^{-1} strain rate. The corresponding mole fraction of H_2 adjacent to the surface, as a function of surface temperature, is shown in Figure 2a. Due to the multiple curves plotted, unstable branches are not shown in dotted lines (as conventionally done). In order to systematically study the role of homogeneous (gas-phase) and heterogeneous (catalytic) chemistries in bifurcation behavior, three problems have been separately examined through numerical experiments: the homogeneous (Homo., dotted line), the heterogeneous (Het., circles), and the coupled homogeneous–heterogeneous (HH, solid line) cases. The homogeneous problem corresponds to an idealized "inert" surface, since radical recombination or generation is known to happen for any real surfaces (Pfefferle and Pfefferle, 1987; Griffin et al., 1989). We should note that the particular surface reaction mechanism does not include radical adsorption to the surface. This coupling mechanism is not yet completely understood (Lewis and von Elbe, 1987; Gray and Scott, 1990). Since radical adsorption followed by recombination usually retards homogeneous combustion (Aghalayam et al., 1998), more work is needed to delineate homogeneous–heterogeneous interactions through surface radical quenching. The heterogeneous case has been realized experimentally under vacuum conditions, and is impossible to achieve experimentally at high pressures.

For the homogeneous problem, an ignition and an extinction occur at ~ 1,000 K. For this fuel-lean mixture, homogeneous combustion can take place only through external energy supply (indicated by positive powers). This behavior is typical for fuel-lean mixtures and is reminiscent of the classical S-curve of Semenov (1935) and Frank-Kamenetskii (1969) for spatially homogeneous and distributed systems.

For the heterogeneous problem, an ignition and an extinction occur at much lower temperatures of ~ 400 K and room temperature, respectively, and startup requires less energy compared to homogeneous combustion. Adiabatic operation is also possible in which the catalyst can self-sustain combustion, that is, on ignition, the system remains reactive (at high temperatures exceeding 2,000 K in this case), even if the heat supply to the catalytic surface is turned off.

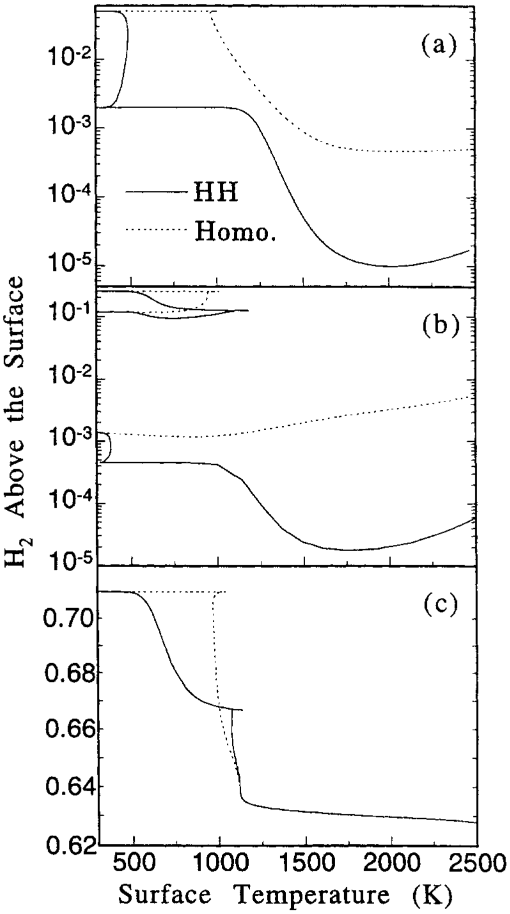

Figure 2. Mole fraction of H_2 above the surface as function of surface temperature.

For fuel-lean (5% H_2 in air, panel a and 25% H_2 in air, panel b) mixtures, a synergism between the surface and gas-phase chemistries leads to higher combustion efficiency and significant fuel reduction. For fuel-rich mixtures (71% H_2 in air, panel c), the catalytic surface serves only as a flame holder at high temperatures. The conditions are 1 atm and 500 s^{-1} strain rate.

Finally, the HH system shows potential for both types of operation, namely exclusively catalytic (or partial oxidation in the case of hydrocarbons) at low temperatures and mainly homogeneous (or total oxidation) at high temperatures. Comparison of the three cases indicates that *at low temperatures (< 1,000 K), combustion is almost exclusively controlled by catalytic chemistry, while at high temperatures (> 1,200 K), homogeneous chemistry dominates.* An interesting feature is that *upon catalytic ignition, the surface reaction exothermicity drives the system directly to the homogeneously ignited branch (flames).* In addition, for the HH case, the onset of homogeneous chemistry occurs at a higher temperature compared to homogeneous combustion alone. This catalyst-induced inhibition on the onset of homogeneous chemistry (or ignition) is desirable in the partial oxidation of hydrocarbons, where the homogeneous chemistry can lead to explosions and reduction of selectivities. This result, if generic, indicates that for systems for which the catalytic chemistry is not well known, *the gas-phase ignition near inert surfaces provides a conservative (or safe) temperature limit for operation of partial oxidation catalytic reactors.* The underlying mechanisms for this inhibition have recently been elucidated by Bui et al. (1996) and Vlachos (1996a).

It is interesting to note that, even at temperatures exceeding 1,500 K, the catalyst still influences reactivity (an HH synergism), as shown by the difference in temperatures between the HH and the "homogeneous only" case at the same power in Figure 1. This synergism leads to significantly lower fuel emissions, as shown in Figure 2a, and improved combustion efficiency due to more complete oxidation of the fuel. This behavior is known as *catalyst-assisted homogeneous combustion,* a term first introduced by Pfefferle and Pfefferle (1986), and is important in the design of advanced gas turbines.

This synergism is unexpected, since at such high temperatures, the coverages of adsorbed species on the catalyst are expected to be low. To clarify this issue, surface coverages of selected species vs. surface temperature are shown in Figure 3a. The results show that prior to ignition, H* is the dominant surface species. Upon ignition, O* is the dominant surface species up to high temperatures, due to its high activation energy of desorption (see Table 2). Figure 4 shows a reaction path analysis, indicating the rates of species adsorption, desorption, and reaction on the surface. Gaseous H_2 and O_2 adsorb dissociatively onto the catalytic surface, forming H* and O*. Due to the high O* surface coverage, H* readily reacts with O* to form OH*, rather than desorbing. This results in an appreciable surface coverage of OH* as shown in Figure 3a. The relatively high concentration of OH* on the surface leads in turn to the formation of water through $2OH^* \rightarrow H_2O^* + H^*$, generating heat and the limiting reactant H* back to the reaction cycle. This net catalytic formation of H_2O generates significant exothermicity, resulting in a higher surface temperature for HH combustion and lower fuel mole fractions (Figure 2a) as compared to the homogeneous combustion alone at the same power.

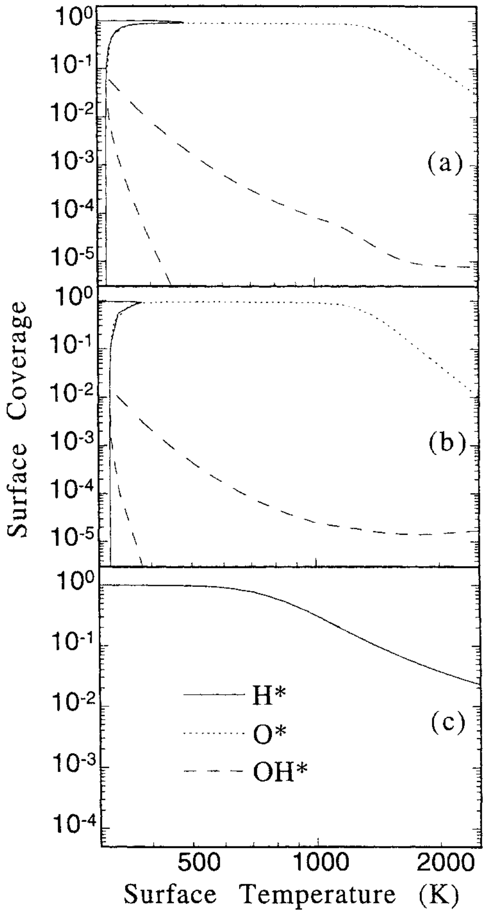

Figure 3. Surface coverage of selected adsorbed species as a function of surface temperature.

Panels a–c are for 5%, 25% (ignited branch only), and 71% H_2 in air, respectively. Vacant sites are the only other dominant species, which are not shown for figure clarity. Conditions are identical to Figure 2.

Fuel-lean mixtures near the stoichiometric point

One-parameter bifurcation diagrams, such as Figure 1, have been studied for the entire compositional regime. An example of a near stoichiometric mixture (25% H_2 in air) is shown in Figure 5, with the corresponding mole fraction of H_2 adjacent to the surface plotted in Figure 2b. Upon catalytic ignition, a direct transition to flames is again found, with a corresponding surface temperature of ~ 2,500 K (these high temperatures can only be envisioned computationally), which would result in catalyst melting (platinum melts at ~ 2,040 K) or possible flame flashback, making direct startup for these compositions dangerous. However, it should also be mentioned that these simulations were performed in the absence of any heat losses (see section on heat loss below), and serve only as limiting cases.

Upon catalytic ignition, the flame burns so vigorously that it is separated from the surface, resulting in a weak surface–flame thermal interaction, so that the homogeneously ignited branch becomes nonextinguishable. As a result, the catalytically and the homogeneously ignited branches are disjoint (see Figure 2b) and the former is not attainable experimentally by simply changing the power. This nonextinction behavior was first reported and analyzed for homogeneous flames a few years ago (Vlachos, 1995), and we observe here that the catalyst does not alter this homogeneous combustion bifurcation feature.

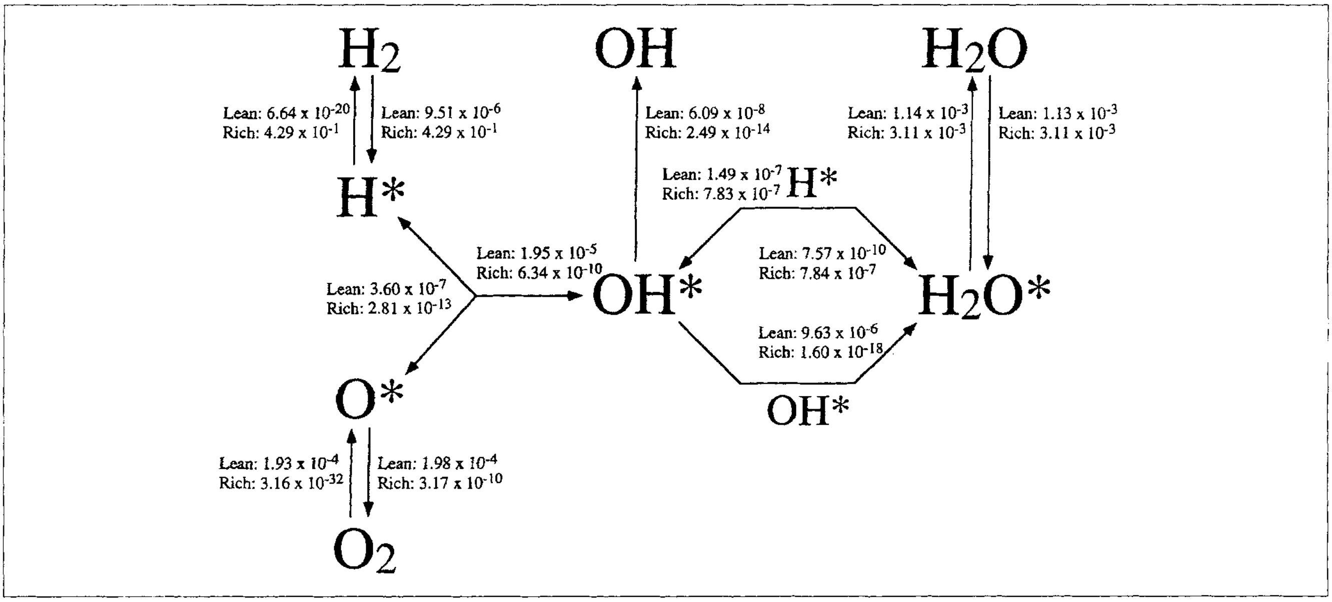

Figure 4. Reaction path analysis on the surface for two compositions of 5% (lean) and 71% H_2 in air (rich).

Arrows indicate the direction of reactions, along with the corresponding rates. The catalyst is much more reactive for fuel-lean mixtures. The conditions are 1 atm and 500 s^{-1} strain rate.

The difference between the catalytically and the homogeneously ignited branches is more clearly shown in Figure 6, in terms of the temperature (panel a) and fuel mole fraction (panel b) profiles, at an identical surface temperature of 1,100 K (corresponding to points A and B in Figure 5). For the catalytically burning flame, the flame is attached to the surface, that is, the highest temperature occurs at the surface. The fuel is depleted from 25% to ~ 12%, and the boundary layer is relatively thin, ~ 0.1 cm. The homogeneously burning flame, on the other hand, is lifted away from the surface, with the maximum temperature of ~ 2,200 K being in the gas phase. Due to these high temperatures in the bulk, fuel reduction is significant, reaching a mole fraction of 10^{-4} at the surface. The boundary layer is also much thicker (~ 0.85 cm) than that of the catalytically burning flame.

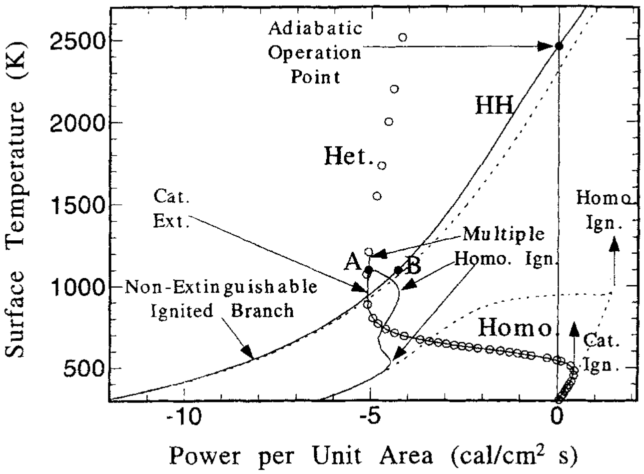

Figure 5. Surface temperature as a function of the power per unit area supplied to the catalytic surface.

For conditions of 25% H_2 in air, 1 atm, and 500 s^{-1} strain rate. For this mixture, startup leads directly to surface melting. The nonextinguishable ignited branch is disjoined from the catalytically ignited branch.

The "homogeneous only" case is also plotted (dotted line) in Figure 6. Comparison with the HH homogeneously ignited branch shows that the profiles are very similar in the bulk. A small inhibition of the gas-phase chemistry due to the catalyst is observed near the entrance. While most of the fuel reduction is caused by homogeneous chemistry in the bulk of the flame, a significant reduction near the surface is caused by heterogeneous chemistry, indicating again an HH synergism.

Our simulations indicate that *even at identical conditions, two very different modes of operation can exist, one that could be potentially interesting for catalytic oxidation and the other one for homogeneous oxidation.* The implications of different reactive branches on operation, as well as control strategies in attaining them (even when the two branches are disjoint) will be discussed below.

Another interesting new feature is that, along the homogeneously ignited branch, the synergism between the surface and gas-phase chemistries changes from moderate at high temperatures to negligible at sufficiently low surface temperatures (Figures 2b and 5). In particular, upon reduction of surface temperature, *a catalyst extinction occurs at a temperature below room temperature at high fuel conversions*, as shown in Figure 2b. Mechanistically, the synergism at high temperatures is due to O* dominating on the surface as shown in Figure 3b, similar to the 5% H_2 in air mixture.

We should note that this catalytic ignition/extinction at low temperatures in the presence of homogeneous combustion is a bifurcation behavior seen for the first time. Such a behavior is at first counterintuitive, because the low-activation-energy catalytic chemistry is expected to light off first and die last compared to homogeneous chemistry. This behavior is due to the spatial nonuniformity of the temperature. Under these

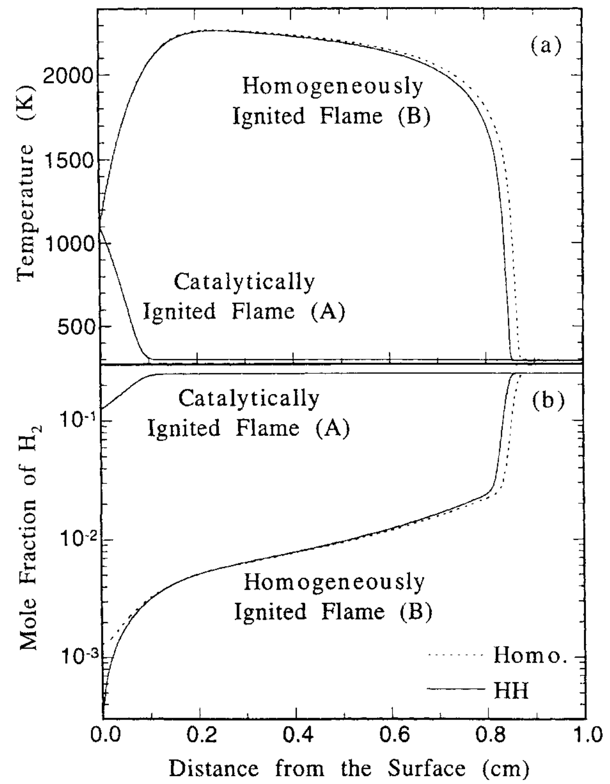

Figure 6. Temperature (panel a) and H_2 (panel b) profiles at conditions identical to Figure 5.

Surface temperature of 1,100 K. The catalytic and homogeneous solutions correspond to points A and B in Figure 5. The homogeneously ignited flame is thick and burns away from the surface in the gas phase, whereas the catalytically ignited combustion is confined in a relatively thin region adjacent to the surface.

conditions, the catalyst serves only as a *flame holder*. Although thermal quenching of the catalyst extinguishes surface chemistry, it has no influence on a surface-stabilized flame for strong flames near the stoichiometric point. As a result, *operation of catalyst-assisted combustors at surface temperatures below catalytic extinction is undesirable.*

Fuel-rich mixtures

Finally, an example of a fuel-rich mixture of 71% H_2 in air is shown in Figure 7, with the corresponding mole fraction of the fuel versus surface temperature shown in Figure 2c. The overall qualitative behavior is similar to results obtained for other compositions. The onset of homogeneous reactivity causes multiple ignitions, resulting from the interactions between the homogeneous and heterogeneous chemistries, and two stable adiabatic operation points, one corresponding to homogeneous combustion (higher temperature) and the second resulting from HH interactions (lower temperature). Another difference from fuel-lean mixtures is the almost identical behavior of the HH combustion to the "homogeneous only" combustion at temperatures greater than ~ 1,200 K, as shown in Figures 2c and Figure 7 (a lack of HH synergism).

Analysis of the surface species coverages (Figure 3c) and of the reaction path, for this fuel-rich condition (shown in Figure 4) indicates that, because H_2 is in excess, almost all of the O_2 is depleted in the gas-phase. Hence the dominant adsorbed species is now H*, but its surface coverage at ~ 1,500 K is only ~ 8%, due to its relatively low activation energy of desorption (see also Table 2), with the rest of the dominant species being vacancies. Consequently, the rate of surface combustion is negligible compared to fuel-lean mixtures, leading to the lack of HH synergism at high temperatures.

We should also note that for a small temperature window the fuel emissions in the "homogeneous only" case are lower than the HH case as shown in Figure 2c. This behavior occurs near the onset of homogeneous chemistry, where the catalyst inhibits homogeneous chemistry (Bui et al., 1996), and can be viewed as a "negative" or undesirable synergism.

Operation Windows for Catalytic and Homogeneous Oxidation and Startup Strategies

The above behavior can be summarized in a two-parameter bifurcation diagram shown in Figure 8. For mixtures near the stoichiometric point, the temperature upon catalytic ignition can exceed 2,000 K (in the absence of heat loss), leading to surface melting, indicating that for safe startup, one must start with a composition below ~ 15% or above ~ 58% H_2 in air.

Upon catalytic ignition, if the heat supply is turned off, the system stabilizes to the adiabatic operation point (thick solid lines). In general, the homogeneously ignited branch corresponds to total oxidation of a fuel, which is desirable for energy production. Therefore, the temperature (or power) window between the adiabatic operation point and the first homogeneous extinction, which occurs as the power is decreased (or at the onset of homogeneous reactivity in the absence of actual turning points), defines the regime for energy production mainly by homogeneous combustion or catalyst-assisted homogeneous combustion, indicated by the shaded region marked as "I". The adiabatic operation curves exhibit a maximum in surface temperature around the stoichiometric point of ~ 29% H_2 in air, exceeding 2,000 K. The homoge-

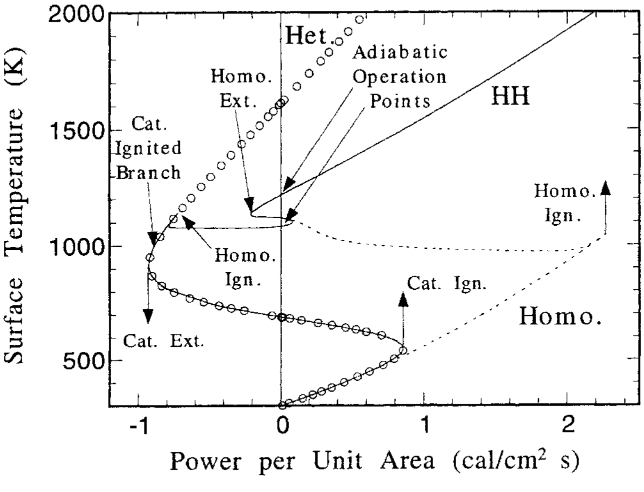

Figure 7. Surface temperature as a function of the power per unit area supplied to the catalytic surface.

For 71% H_2 in air, 1 atm, and 500 s^{-1} strain rate. Interactions between homogeneous and heterogeneous chemistries result in multiple distinct adiabatic operation points. At high temperatures, the catalyst has no influence on homogeneous combustion.

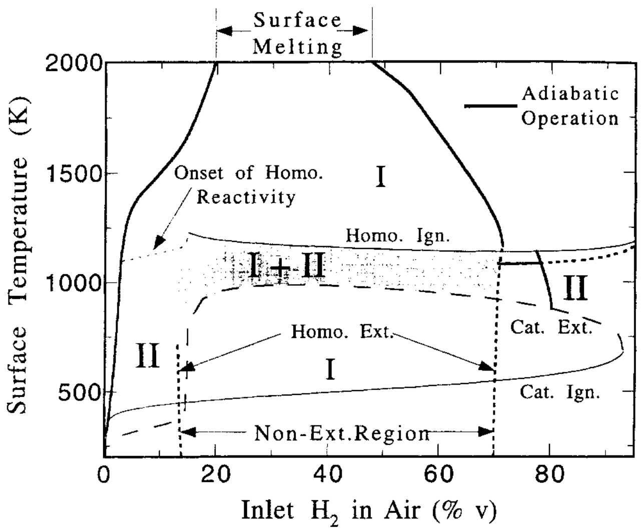

Figure 8. Regions for catalytic and homogeneous oxidation as a function of fuel composition.

Conditions identical to Figure 1. Shaded region I indicates the regime for homogeneous (total) oxidation, shaded region II indicates the regime for catalytic (partial) oxidation, and shaded region I + II indicates a combined temperature regime for either catalytic or homogeneous oxidation.

neous extinction temperatures (thick dotted lines) show much more complex behavior. For compositions between ~ 14% and ~ 70% H_2 in air, the ignited flame cannot be extinguished, and thus energy can be extracted without loss of flame stability by thermal quenching. An example corresponding to the homogeneously ignited branch is shown in Figures 5 and 6.

For compositions in which homogeneous extinction is possible (less than ~ 14% and greater than ~ 70% H_2 in air), extraction of energy beyond the homogeneous extinction point leads the system to the catalytically ignited branch, between the catalytic extinction point and the first homogeneous ignition point as indicated in Figure 7 (or the onset of homogeneous reactivity in the absence of actual turning points as shown in Figure 1). Usually, the catalytically ignited branch corresponds to partial oxidation of a fuel, and determines the operation regime for chemical synthesis in the case of hydrocarbons. This region of catalytic oxidation is shown as a function of fuel composition in Figure 8, indicated by the shaded region marked as "II".

For mixtures near the stoichiometric point, the operation temperature windows for catalytic and homogeneous oxidation can coincide, as marked by the shaded region "I + II". However, this multiplicity in operation mode is associated with different physical situations, as shown in Figures 5 and 6.

Figure 8 also gives insight into actual control strategies to attain desired operation regimes. A possible strategy to attain either the homogeneous oxidation or the catalytic oxidation mode, even when the two branches are disjoint, is as follows. One can start up at a safe composition, such as 5% H_2 in air. Upon catalytic ignition, the catalyst can be quenched to the desired temperature and branch (either homogeneously ignited in regime I or catalytically ignited in regime II) by controlling the amount of energy exchanged. Then, the composition of the fuel can be increased, while controlling the temperature through heat exchange. The composition can then be selected so that minimum pollutant emissions occur, in the case of energy production, or best selectivities to partially oxidized products are achieved, in the case of hydrocarbons. Thus, bifurcation diagrams such as Figure 8 and associated control strategies can be invaluable engineering tools for all applications.

Influence of Catalyst on Adiabatic Operation and Flammability Limits

Technically, even though the adiabatic limits of operation are not the flammability limits (for a definition see Lewis and von Elbe, 1987), they define the lowest and highest fuel compositions within which self-sustained combustion can occur. In that context, the adiabatic operation limits can be thought of as flammability limits for flow reactors. This approach has been adapted by other researchers as well (see, for example, Veser and Schmidt, 1996), whose experimental data show good agreement with actual literature flammability limits.

The effects of the catalyst on the loci of adiabatic temperature (panel a) and the fuel mole fraction just above the surface (panel b) as a function of inlet fuel composition are shown in Figure 9, for both the "homogeneous only" and the HH cases. Homogeneous combustion alone (dotted line) can be sustained only in the composition range of ~ 7% to ~ 70% H_2 in air. For heterogeneous combustion alone (circles), the system can operate adiabatically over a wider range of compositions, from below 1% to ~ 80% H_2 in air. Recent experiments in our laboratory confirm the observation that combustion can be self-sustained down to very fuel-lean mixtures (Fernandes et al., 1998). The results show that for relatively low adiabatic temperatures (found for sufficiently fuel-lean and fuel-rich mixtures), HH combustion is primarily controlled by surface reactions. On the other hand, at the higher adiabatic temperatures near the stoichiometric point, HH combustion is mainly controlled by homogeneous chemistry. The three distinct loci of adiabatic operation points for the HH case are shown in Figure 9a at fuel-rich conditions, corresponding to heterogeneous combustion alone, HH combustion, and homogeneous combustion, as the inlet H_2 composition decreases.

To delineate the thermal vs. kinetic role of surface chemistry in flammability limits, a numerical experiment was performed. The squares in Figure 9a show results for a simulation in which the HH case was considered, but with the heats of the surface reactions set to zero. The similarity between the homogeneous case and this modified HH process indicates that *the heat generated by surface reactions is responsible for the expansion of the flammability limits, rather than details of the complex surface reaction mechanism.* In fact, the HH case with the heats of reactions turned off shows a higher fuel-lean flammability limit compared to the "homogeneous only" case, indicating that catalytic reactions actually retard adiabatic behavior. This kinetic inhibition of the fuel-lean flammability limit by the catalytic surface is probably due to the surface formation of H_2O, which can inhibit H_2 flames due to the enhanced collisional efficiency of H_2O in the chain-termination reaction, $H + O + H_2O \rightarrow HO_2 + H_2O$ (for a more detailed analysis of H_2O retarding effects, see Vlachos, 1995). Furthermore, the additional two loci of adiabatic operation

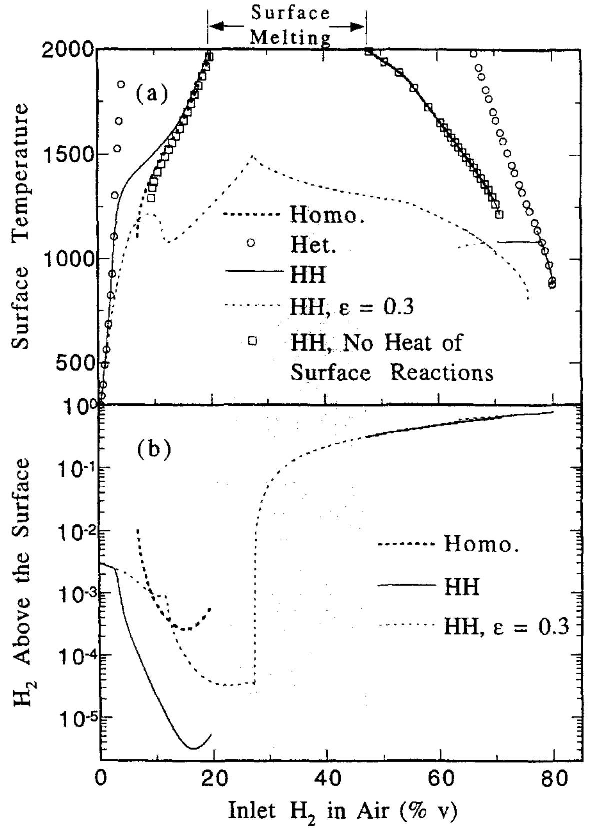

Figure 9. Panel a—adiabatic or autothermal temperature loci as a function of fuel composition; panel b—fuel emissions above the surface.

Panel a is for conditions of 1 atm and 500 s^{-1} strain rate for the different cases indicated. The heat generated by the surface reactions is responsible for the expansion of both the fuel-lean and rich flammability limits. Panel b is for the HH and "homogeneous only" case. HH synergism occurs only for fuel-lean conditions.

(between ~ 75% and 80%) also disappear in the absence of heat from catalytic reactions.

HH synergism in adiabatic temperature and fuel emissions occurs only for fuel-lean conditions, as shown in Figure 9a. Interestingly, even though there is not much difference in adiabatic temperature between HH and "homogeneous only" combustion for fuel-lean mixtures near the stoichiometric point, the HH system significantly reduces the fuel near the surface (by over two orders of magnitude near ~ 20% H_2 in air). This behavior shows that for some conditions a catalyst can substantially reduce pollution while having negligible influence on the surface temperature. The change in HH synergism with inlet composition is due to a change in the dominant surface species on the surface and homogeneous combustion efficiency, as discussed in Figure 4, along with a change in surface temperature.

Effect of Heat Loss on Bifurcation Behavior

In the aforementioned results, heat losses from the surface were not considered. Figure 10 shows the effect of radiative heat loss from the catalytic surface (emissivity of $\epsilon = 0.3$ (Warnatz et al., 1994)) for two different fuel compositions of 5% (panel a) and 71% (panel b) H_2 in air. For both compositions, radiative heat loss decreases the autothermal surface temperature, especially at high temperatures, so surface melting is not a problem at steady-state. Even though heat loss does not qualitatively alter the bifurcation features, it shifts the homogeneous ignition to a higher power. As a result, the catalytically ignited branch can now be directly accessed upon catalytic ignition. In addition, heat loss shrinks the loci of adiabatic operation, especially the fuel-rich flammability limit, as shown in Figure 9.

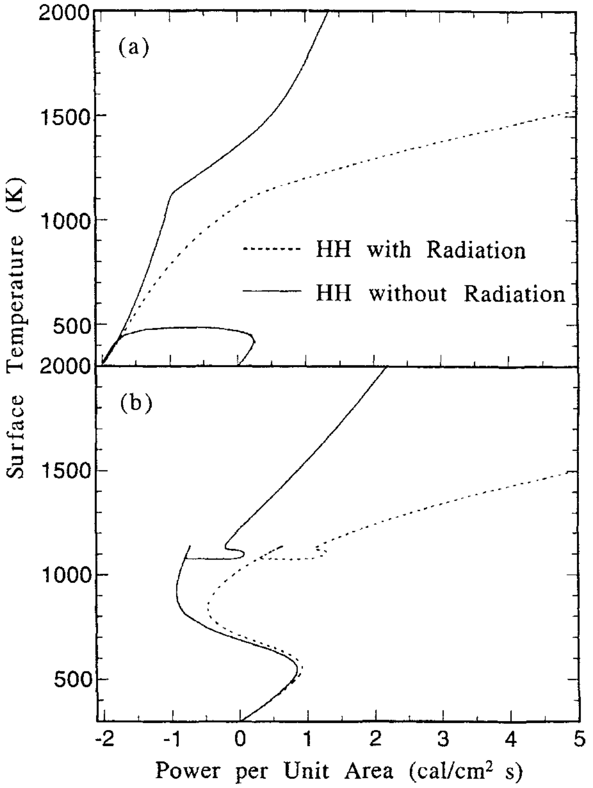

Figure 10. Surface temperature as a function of the power per unit area.

For conditions of 1 atm, 500 s^{-1}, and two fuel compositions of 5% (panel a) and 71% H_2 (panel b) in air. Solid lines indicate no heat loss, while dotted lines indicate radiative heat loss from the surface with an emissivity of 0.3. Radiative heat loss does not qualitatively alter the bifurcation behavior, but considerably promotes accessibility of the catalytically ignited branch.

Conclusions

The effects of homogeneous and heterogeneous chemistries on the homogeneous–heterogeneous synergism and operation regimes in a spatially distributed stagnation microreactor were studied for H_2/air mixtures. It was shown that at low temperatures the surface chemistry dominates almost exclusively, whereas at high temperatures homogeneous chemistry is more important. The combined effect of homogeneous and heterogeneous reactions facilitates startup, can result in coexistence of both catalytically and homogeneously ignited branches, and expands the fuel-lean and rich flammability limits. HH synergism regarding fuel emissions occurs at elevated temperatures, but only for fuel-lean mixtures. Surprisingly, for nonexistinguishable mixtures near the stoichiometric point, the HH synergism decreases as the surface temperature decreases toward the catalytic extinction, beyond which only homogeneous chemistry occurs in the bulk of the flame. This aspect has important implications for integrated heat exchanger/combustor systems, where the catalyst activity may be lost at sufficiently low surface temperatures.

Temperature/composition operation windows for energy production and catalytic oxidation were identified using continuation techniques, and a possible control strategy to attain various operation regimes was discussed. Kinetically, the catalyst slightly inhibits adiabatic operation, and the heat generated by surface reactions is the key factor in the expansion of flammability limits. Surprisingly, catalytic ignition leads directly to flames and possible catalyst melting over a wide range of compositions in the absence of heat loss. Surface radiation was found to be important for a direct transition from the heat extinguished to a catalytically ignited branch.

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