Gas Phase and Catalytic Ignition of Methane and Ethane in Air over Platinum

The ignition of gas phase combustion by a heated catalytically active surface involves dynamic coupling of transport processes and chemical kinetics. Researchers have observed that surfaces with high catalytic activity require higher surface temperatures to ignite gas phase combustion, compared to nonactive surfaces, and that this difference is greatest for a stoichiometric mixture. In this work an analysis of the ignition of surface-catalyzed oxidation is developed along with an experimental technique for independently monitoring both surface and gas phase ignition such that the dynamics of these two events can be decoupled. Experiments suggest that the sharp maximum in surface temperature required for gas phase ignition observed in previous work is an artifact caused by transient heating of the surface as ignition occurs. Analysis of surface ignition was also used to investigate the kinetics of methane and ethane oxidation on platinum.

Timothy A. Griffin
Lisa D. Pfefferle
Yale University
Department of Chemical Engineering
New Haven, CT 06520

Introduction

Sixty years ago, Coward and Guest (1927) studied the ignition of stagnant natural gas-air mixtures over electrically heated catalytic and noncatalytic metal bars. They found that the surface temperature required for gas phase ignition was higher for surfaces that were active for catalytic oxidation of natural gas than for noncatalytic surfaces. Data obtained by Coward and Guest, (Figure 1) indicate that the ignition temperature for catalytic surfaces goes through a sharp maximum at the stoichiometric fuel-air mixture (assuming complete combustion) when plotted against the fuel/air ratio. This type of behavior was not observed for surfaces that are less active for catalytic oxidation of natural gas, such as stainless steel or nickel. The sharp maximum in surface temperature required to ignite a natural gas-air mixture over a platinum surface at an equivalence ratio of 1 is of interest because, if real, it indicates a change in a surface reaction characteristic related to the bulk equivalence ratio, which consequently influences gas phase reactivity. (Equivalence ratio is defined as the actual fuel/air ratio divided by the stoichiometric fuel/air ratio, assuming complete oxidation for reaction to CO_2 and H_2O. A mixture with excess air $[\phi < 1]$ is referred to as lean; a mixture with excess fuel $[\phi > 1]$ is referred to as rich.)

In the decades following their publication, Coward and Guest's results have appeared in the literature frequently (Jost, 1946; Laurendeau, 1982; Lewis and von Elbe, 1987). Initial experiments in our lab that were performed to study gas phase ignition of methane and methane-ethane mixtures over Pt and Pd foils confirmed the observations of Coward and Guest. Our results obtained for the ignition of methane and 20% ethane–80% methane fuels are shown in Figure 2. This methane-based fuel mixture (simulated natural gas) exhibits a sharp maximum in platinum or palladium surface temperature required for gas phase ignition for a stoichiometric mixture. The location and width of this sharp maximum are both similar to those obtained by Coward and Guest. Our results for ignition of ethane and methane-air mixtures over nickel surfaces showed no such sharp maximum, again consistent with Coward and Guest.

A higher required surface temperature for gas phase ignition over a catalytic surface (compared with a noncatalytic surface) can be explained by examining the local concentration of reactants adjacent to the heated surface. For surface temperatures sufficiently high for gas phase ignition, surface oxidation reactions will be mass transfer limited. During ignition of the surface oxidation reaction (defined as the transition to a mass transport limited surface reaction rate) the composition of gas adjacent to the catalyst surface changes dramatically, with the concentration of the limiting reactant approaching zero at the wall. Thus, the local equivalence ratio near the surface is changed: a lean mixture is made learner, a rich mixture is made

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Correspondence concerning this paper should be addressed to L. D. Pfefferle.

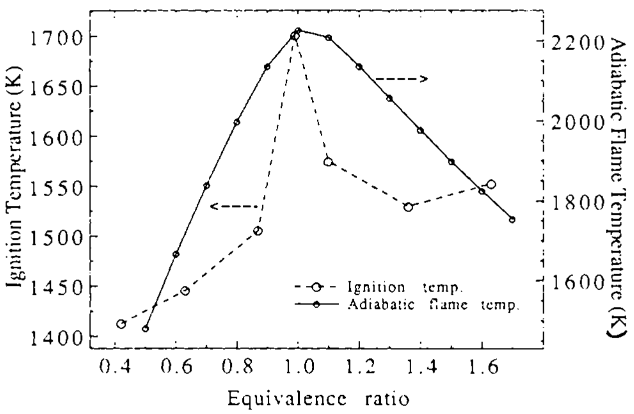

Figure 1. Coward and Guest (1927) ignition data (for natural gas) and methane adiabatic flame temperature as a function of fuel/air equivalence ratio.

richer as fuel and oxidizer are converted into products on the surface. At the stoichiometric condition both fuel and oxygen are depleted and can be reduced to low concentrations near the surface. Depletion of the limiting reactant(s) lowers the reactivity of the gas near the surface, increasing the surface temperature required for gas phase ignition. Note that although the surface temperature required for ignition can be higher over the catalytically active surface, the externally supplied power required to maintain the surface at the ignition temperature can be significantly less than that for a noncatalytic surface due to heat released by exothermic surface reactions.

The sharp increase in surface temperature required for gas phase ignition of natural gas-air mixtures at an equivalence ratio ϕ of 1 has been explained by postulating a maximum in catalytic reaction rate at this condition (Lewis and von Elbe, 1987). There is, however, no experimental evidence to suggest a sharp maximum in surface reaction rate at $\phi = 1.0$. Mass transport limited surface oxidation implies a linear dependence of the rate on bulk concentration of the limiting reactant, which would result in a maximum rate at $\phi = 1.0$.

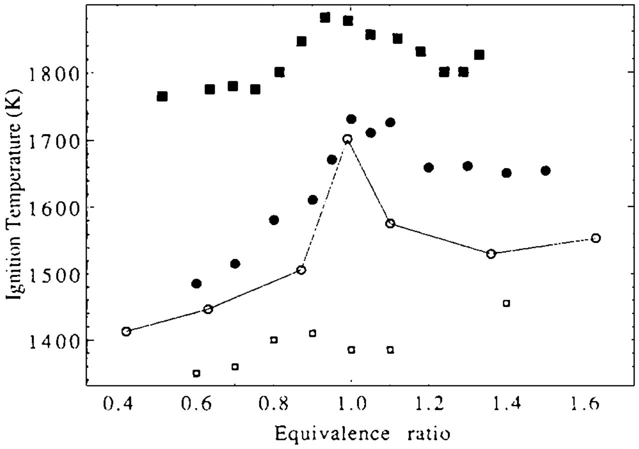

Figure 2. Gas-phase ignition of methane-air and 20% ethane–80% methane/air by heated metal foils.

- ⊖ Coward and Guest (1927), natural gas, Pt
- ● 20% ethane–80% methane, Pd
- ☐ 20% ethane–80% methane, Ni
- ■ Pure methane, Pt

The peak in the gas phase ignition temperature at $\phi = 1$ for Pt surfaces could also be explained by the catalytic production of ignition-enhancing reaction products, the chemical identity and production rates of which can be a strong function of bulk stoichiometry. There is previous experimental evidence that demonstrates how the products of the surface oxidation reaction can affect the ignitability of the gas layer near the surface. As investigated in our earlier work on the effect of catalytically produced radicals on gas phase ignition (Pfefferle et al., 1989a,b; Griffin et al., 1989), ignition-enhancing species such as OH and O can, for lean equivalence ratios, lead to a lower required surface temperature for gas phase ignition over a platinum surface as compared to a quartz surface. This effect can also significantly widen the gas phase combustion stability limits and allowing stabilization of ultralean mixtures ($\phi = 0.08$ demonstrated for ethane/air). We have verified OH emission from platinum and demonstrated its role in stabilizing gas phase combustion both at atmospheric (Pfefferle et al., 1988; Griffin et al., 1989) and subatmospheric (Griffin et al., 1988) conditions. Ethane, for example, exhibits significant lean ignition enhancement over platinum, as illustrated by our boundary layer experiments using OH radical measurement as a combustion indicator (Pfefferle et al., 1989).

Research on the hydrogen-oxygen system gives further evidence for direct surface OH radical production on platinum. Experiments were performed at low pressure (~0.1 torr) with no diffusion limitation and OH production rate was found to be a strong function of stoichiometry (Hsu et al., 1986, 1987; Hellsing et al., 1987; Ljungström et al., 1987). These studies found that the apparent activation energy for OH production decreased as the surface coverage of oxygen is increased (a value of ~125 kJ/mol was obtained near the lean limit). Modeling of the surface oxidation reaction by Hellsing and Kasemo (1988) provides insight into the reaction mechanism responsible for radical production. The surface coverage of intermediates (O, OH on the lean side, H on the rich side) was calculated to increase dramatically as the surface is made leaner or richer than stoichiometric.

The results of the above cited work can be generalized into the following hypothesis, relevant for high-temperature, surface-catalyzed oxidation reactions.

> When there is an excess of reactant (either fuel or oxidizer), intermediates—OH radicals, products of incomplete oxidation (CH_2O, CO, H_2, hydrocarbon radicals)—may desorb in sufficient fluxes to affect the gas phase ignition process.

Alternatively, for stoichiometric conditions intermediate coverages should be small and their desorption unlikely. A change in the surface reaction product distribution with fuel/air ratio changes the reactivity of the fuel-air mixture near the surface. This explanation does predict the decrease in platinum surface temperature for lean gas phase ignition as well as the maximum in ignition temperature at $\phi = 1$ because radical desorption is less likely, but again does not necessarily predict that this maximum should be sharp.

Experimental Overview

Possible experimental biases leading to an apparent ignition temperature maximum at $\phi = 1.0$ must be considered. In both

Coward and Guest's work and our confirmation experiments, the surface ignition event was not recorded; thus, it is possible that gas phase ignition could have occurred in the course of the transient heating of the metal surface during the transition from kinetic to mass-transport control. If the surface were adiabatic (i.e., no radiative or conductive losses and no external heating) and $Le = 1$, the surface temperature would reach the adiabatic flame temperature (Satterfield et al., 1954), which is significantly higher than the ignition temperature. For a nonadiabatic surface during surface ignition (transfer to mass transfer limited operation), the final steady-state temperature will be lower than the adiabatic flame temperature. Heat transfer from the surface, however, is controlled by a relatively slow diffusive process. Under these conditions (τ reaction $\ll \tau$ diffusion), there can be a significant overshoot in the surface temperature with respect to steady state. In this situation the surface temperature could have risen to a temperature higher than that required to ignite the adjacent gas due to the different time scales corresponding to the heating of the metal and the heating of the gas. (We did observe an abbrupt jump in surface temperature preceding ignition of the gas in our experiments with platinum and palladium.) A maximum excursion would be expected at the stoichiometric condition that corresponds to the maximum adiabatic flame temperature for methane-air. In Figure 1 the adiabatic flame temperature of methane-air mixtures as a function of ϕ is plotted along with the Coward and Guest data for surface temperature required for gas phase ignition. The maxima occur in approximately the same position with respect to fuel/air ratio although the adiabatic flame temperature has a much broader maximum.

Thus, we have the question as to whether the apparent sharp peak in required surface temperature near $\phi = 1$ is an artifact caused by gas phase ignition occurring during the surface ignition event. In order to construct a coupled heterogeneous-homogeneous reaction mechanism model to numerically investigate this phenomenon, high-temperature surface oxidation rate data are required. An analysis of the surface ignition data obtained in this study was developed and applied and results compared with those of previous investigations (Cho and Law, 1986; Hiam et al., 1968; Trimm and Lam, 1980).

In order to eliminate intrusion from transients introduced by surface ignition, we developed an experimental system and analysis method to monitor and separate the gaseous and surface ignition events. The theory of ignition of surface reactions (the transition from kinetic to mass-transport control of the reaction rate) is developed and applied to the yield information on the intrinsic kinetics of high-temperature platinum-catalyzed oxidation of methane and ethane. This follows the work of Cardoso and Luss (1969), Cho and Law (1986), and Hiam et al. (1968). In addition, the relationship between the ignited state (mass transport limit) and the original state (intrinsic kinetic limit) is discussed in connection with the gas phase ignition of methane and ethane by heated catalyst surfaces. The decoupled gas phase ignition experiments were performed for methane-air mixtures. No sharp maximum was observed at the stoichiometric ratio, although we did observe a decrease in ignition temperature on the lean side. This lean promotion was expected from our earlier work on the formation of oxidizing radicals over platinum surfaces, which is more pronounced for lean equivalence ratios (Pfefferle et al. 1989a,b; Griffin et al. 1989). The absence of a sharp maximum in gas phase ignition temperature at the stoichiometric ratio when surface and gas phase ignition events are separated suggests that transient heating effects during the surface ignition event were likely responsible for the peak observed by previous investigators.

Experiments were designed

1. To measure the high-temperature surface kinetics for methane and ethane combustion to quantify the transition to mass transfer limited rate
2. To determine the conditions for gas phase ignition under more easily modeled, steady-state transport conditions (i.e., with minimal intrusion of wire temperature transients).

Experimental details are described below.

Apparatus and procedures

Surface ignition experiments were performed with a design adapted from that of Cho and Law (1986) and Hiam et al. (1968). The design was optimized to allow accurate measurement of the surface ignition temperature and the energy deposited on the catalyst by the mass transport limited surface reaction.

The apparatus consists of a Wheatstone bridge composed of two catalyst filaments (wires) of equal resistance (76 to 250 μm dia. ~3.5 cm long), one placed in the reactant stream, the other in an unreactive stream of air. The remainder of the bridge contains two fixed 1 ohm resistors. During experimentation, the wire temperatures were increased slowly by raising the circuit voltage. At ignition, the energy deposited by the reaction raises the resistance of the "active" wire, causing a voltage drop across the bridge. The circuit voltage was held constant after ignition and the wire resistance and voltage drop increased as ignition spread throughout the wire. The temperature of the wire at ignition is determined from its resistance, utilizing the known temperature-resistance correlations for the metal (Brandes, 1983; Nordine et al., 1973). In turn, the wire resistance, R_w, is found through measurement of the voltage drop across and current through the wire and application of Ohm's law. The current was found by measuring the voltage drop across a small 0.0021 ohm resistor in series with the catalyst. Computerized data acquisition hardware and software monitored the voltage across the 0.0021 ohm resistor, bridge, and catalyst at 0.5 s intervals. The energy required to maintain a given wire temperature is found through $i^2R_w = V^2/R_w$. After ignition, the energy deposited by surface reaction per unit time is the difference between V^2/R_w values determined experimentally with and without fuel. It is assumed that the dissipated chemical energy of oxidation is randomized; that is, that the desorbed products are in equilibrium with the surface, characterized by the surface temperature.

The chemical state of the platinum surface was unknown; however, one indication of its uniformity was the reproducibility of our ignition data. It has been shown by Keck et al. (1983) that the ignition temperature correlates with the presence of surface impurities. Thus, the reproducibility of ignition temperature is a good indicator for the consistency of surface properties, if not surface cleanliness. For the ignition of hydrogen oxidation on platinum at atmospheric pressure, Keck et al. found an increase from 333 to 423 K as the surface became covered with Si and O, as measured by Auger electron spectroscopy. They also determined that the most effective way to remove this impurity, that is, to activate the catalyst, was to heat the platinum in a H_2–O_2

mixture rather than in a reducing H_2 atmosphere. Therefore our reported data were obtained after activating the platinum wire by flowing an ultra-lean methane or ethane mixture over the wire, which was held at such a high temperature that the surface raction was ignited.

Flows over the catalyst wires were kept in the low *Re*, or creeping flow regime, as recommended by Cho and Law (1986). In this range, approximate axisymmetry of the flow and transport exists such that the catalytic response is uniform over the wire surface provided that there are minimal temperature gradients along the wire. If the *Re* were large the complications of boundary layer development, flow separation, and recirculation would make transport nonuniform and the analysis of ignition more complicated.

The uniform, low *Re* laminar flows were created by a 3 in dia. cylindrical flow distributor, filled with 4 mm dia. glass beads to promote mixing, followed by a honeycomb monolith of small channels through which the gas exited. This distributor is similar in design to a typical flat flame burner and has been tested for flow uniformity using hot wire anemometry. Velocities in the range of 3–10 cm/s were used corresponding to $Re < 1$.

Analysis of surface ignition

The surface temperature required for gas phase ignition is determined by balancing of thermal and mass transport and reaction rates and thus is a function of local stoichiometry, residence time, and the dimensionless mass transport coefficient. Because exact similarity in all of these parameters is difficult to achieve, gas phase ignition temperatures are system specific.

The conservation equations for species and energy for the condition of low *Re* flow over a catalytic wire can be expressed as,

$$\frac{dC_{\sigma i}}{d\theta} = \frac{Nu_m D_i}{d_w}(C_{gi} - C_{\delta i}) + \nu_i r(C_\sigma, T_\sigma) \qquad (1a)$$

and

$$\frac{A}{P}\rho\, C_p \frac{dT_\sigma}{d\theta} = -\frac{Nu_h k}{d_w}(T_\sigma - T_g) - \dot{q}''_{\text{rad}} + \frac{i^2 R_w}{PL} + \nu_1 r(C_\sigma, T_\sigma)(-\Delta H) \qquad (2)$$

which are both written for exposed surface area *PL*, where *P* is the perimeter of the wire and *L* is the length. The energy equation is written for the catalyst wire. The species conservation equation is written for the two-dimensional catalyst surface. As written, there are two concentration variables: $C_{\sigma i}$, the concentration of species *i* on the surface (mol/cm^2), and $C_{\delta i}$, the concentration of species *i* in the gas adjacent to the surface (mol/cm^3). C_{gi} is the bulk concentration of species *i* and the vector C_σ represents all of the species participating in the surface reaction. It is assumed that there is a one-to-one correspondence between $C_{\sigma i}$ and $C_{\delta i}$. To analyze the stability of these equations an analytic expression relating these two concentrations must be assumed. The simplest such assumption is that the surface and adjacent gas phase concentration are linearly related to one another through an equilibrium constant K_i. This assumes equilibrium and low surface coverage (a good assumption for the fuel component but not for the oxidizer). *A* is the cross-sectional area of the wire, the other symbols are defined in the Notation.

If we assume that $C_{\sigma i} = K_i C_{\delta i}$, the species conservation becomes:

$$\frac{dK_i C_{\sigma i}}{d\theta} = \frac{Nu_m D_i}{d_w}(C_{gi} - C_{\delta i}) + \nu_i r(C_\sigma, T_\sigma) \qquad (1b)$$

If we further assume that the constant K_i remains unchanged during any transient (i.e., that it is a weak function of temperature or composition in the range expected) the following is obtained:

$$\frac{dC_{\delta i}}{d\theta} = \frac{Nu_m D_i}{K_i d_w}(C_{gi} - C_{\delta i}) + \frac{\nu_i}{K_i} r(C_\sigma, T_\sigma) \qquad (1c)$$

The heat removal data for nonreactive flow as a function of wire temperature were measured and were modeled with a fourth-order least-squares fit to account for the curvature at high temperatures. (The polynomial expression also accounts for conductive heat loss from the catalyst wire to its brass supports.) Since the wire temperature was maintained, in part, by electrical current in our experiments, a V^2/R_w term also appears in the energy equation.

Thus in our energy balance, the polynomial expression,

$$\frac{Nu_h k}{d_w}(T_s - T_g) + \dot{q}''_{\text{rad}} = \frac{1}{PL}\sum_{j=0}^{4} \alpha_j T_s^j \qquad (3)$$

is employed for the rate of heat removal from the wire, because both radiation and natural convection play a large role at the low *Re* conditions, especially at high temperatures. Over our range of operating conditions, $Ra_h = 0.0002$–0.02 and $(Ra_h Pr)^{1/4} = 0.10$–0.35. Both conservation equations contain a source term resulting from the catalytic surface reation, $r\,(C_\sigma, T_\sigma)$. To solve the system of differential equations a rate expression must be determined. In our experiments, air was used as the oxidizer. The variation of oxygen concentration was small over our range of operating conditons: the O_2 mole fraction changes only 10% (from 0.21 to 0.19) as the methane/air equivalence ratio is increased from 0 to 1. The corresponding variation for the ethane/air equivalence ratio is less. An oxygen reaction order less than 1 will further reduce the effect of oxygen concentration on the reaction rate. For these reasons, an effective first-order rate expression was used in our analysis of surface ignition, based on the concentration of fuel (species 1) at the interface, $r = \nu_i k_{eff} C_\delta$.

Using the assumption of first-order kinetics, the fuel and energy conservation equations become (assuming $\nu_1 = 1$):

$$\frac{dC_\delta}{d\theta} = \frac{Nu_m D_1}{K_1 d_w}(C_g - C_\delta)\,\frac{k_{eff}\, C_\delta}{K_1} \qquad (5)$$

$$\frac{A}{P}\rho\, C_p \frac{dT_\sigma}{d\theta} = -\frac{1}{PL}\sum_{j=0}^{4} \alpha_j T_s^j + \frac{i^2 R}{PL} + k_{eff}\, C_\delta(-\Delta H) \qquad (6)$$

In this and subsequent equations the subscript i is dropped from the species variable and all species balances will be for the fuel component. These conservation equations are similar in form to those obtained for a continuous stirred-tank reactor (CSTR). In addition, the species conservation equation is similar to that obtained by Cardoso and Luss (1969) in their comprehensive account of surface ignition by catalytic wires. However, they did not distinguish between gas phase concentration adjacent to the surface and the surface concentration (or coverage), and thus their formulation is not dimensionally consistent. This system of ordinary differential equations can be linearized and its stability analyzed following the classical procedure outlined by Bilous and Amundson (1955) and employed by Cardoso and Luss (1969). The equations are linearized by taking their first-order Taylor series about a steady state corresponding to surface temperature $T_{\sigma,s}$ and species 1 concentration in the gas adjacent to the surface, $C_{\delta,s}$. The linearization is done by introducing the variables,

$$c = C_{\delta,s} - C_\delta \tag{7}$$

$$t = T_{\sigma,s} - T_\sigma \tag{8}$$

The linearized equations take the form,

$$\frac{dc}{d\theta} = -a_{11}c - a_{12}t \tag{9}$$

$$\frac{dt}{d\theta} = -a_{21}c - a_{22}t \tag{10}$$

with coefficients

$$a_{11} = \frac{Nu_m D_1}{K_1 d_w} + \frac{z}{K_1} e^{-E/RT_{\sigma,s}} \tag{11}$$

$$a_{12} = \frac{C_{\delta,s}}{K_1} \frac{E}{RT^2_{\sigma,s}} z e^{-E/RT_{\sigma,s}} \tag{12}$$

$$a_{21} = \frac{-Pz(-\Delta H)}{A\rho C_p} e^{-E/RT_{\sigma,s}} \tag{13}$$

$$a_{22} = \frac{-zC_{\delta,s}EP(-\Delta H)e^{-E/RT_{\sigma,s}}}{A\rho C_p RT^2_{\sigma,s}} - \frac{1}{AL\rho C_p}\left[\frac{\partial(i^2R_w)}{\partial T}\right]_{C_{\delta,s},T_{\sigma,s}} + \frac{1}{AL\rho C_p}\sum_{j=0}^{4} j\alpha_j T^{j-1}_{\sigma,s} \tag{14}$$

in which it is assumed that the temperature dependence of $Nu_m D_1$ can be neglected in comparison with that of k_{eff}, which follows Arrhenius behavior, $k_{eff} = z\exp(-E/RT)$.

Since solution of these linearized equations occurs in the form of exponentials, the following stability criteria must be met:

$$a_{11}a_{22} - a_{12}a_{21} > 0 \tag{15}$$

$$a_{11} + a_{22} > 0 \tag{16}$$

The first condition is often referred to as the "slope criterion":

$$\frac{1}{AL\rho C_p}\sum_{j=0}^{4} j\alpha_j T^{j-1}_{\sigma,s} > \frac{\dfrac{zC_{\delta,s}EP(-\Delta H)e^{-E/RT_{\sigma,s}}}{A\rho C_p RT^2_{\sigma,s}}}{1 + \dfrac{d_w z e^{-E/RT_{\sigma,s}}}{Nu_m D_1}} + \frac{1}{AL\rho C_p}\left[\frac{\partial(i^2R_w)}{\partial T}\right]_{T_{\sigma,s}} \tag{17}$$

This can be interpreted physically as requiring the slope of the heat removal curve (that is, its gradient with respect to the surface temperature) to be greater than that of the heat generation curve, which includes a resistive heating component. The form of the electrical power term in $i^2R_w = V^2/R_w$ is dependent upon whether the resistive heating is carried out under constant current or constant voltage. Constant-voltage heating (power $= V^2/R_w$) was applied in our experiments and is under most conditions more stable since increases in wire temperature act to reduce its magnitude. Specifically, under constant-voltage heating

$$\frac{\partial(V^2/R_w)}{\partial T} < 0 \tag{18}$$

due to increase in wire resistance with temperature. The denominator in the first term on the righthand side of inequality of Eq. 17 accounts for mass transfer limitations in the surface reaction rate. When the reaction is under kinetic control,

$$\frac{d_w z e^{-E/RT_{\sigma,s}}}{Nu_m D_1} \ll 1 \tag{19}$$

and the denominator of the first term on the righthand side of Eq. 17 is unity, simplifying the expression.

The second condition for stability is

$$\frac{1}{AL\rho C_p}\sum_{j=0}^{4} j\alpha_j T^{j-1}_{\sigma,s} + \frac{Nu_m D_1}{K_1 d_w}\left(1 + \frac{d_w z e^{-E/RT_{\sigma,s}}}{Nu_m D_1}\right) > \frac{zC_{\delta,s}EP(-\Delta H)e^{-E/RT_{\sigma,s}}}{A\rho C_p RT^2_{\sigma,s}} + \frac{1}{AL\rho C_p}\left[\frac{\partial(V^2/R_w)}{\partial T}\right]_{T_{\sigma,s}} \tag{20}$$

This is implied by the first condition—inequality of Eq. 17–if we are in the regime of kinetic control defined by Eq. 19. Thus, it is the first condition that will govern the occurrence of the kinetic↔mass transfer transition (surface ignition). Formally, the second condition will be implied by the first if,

$$\frac{zC_{\sigma,s}EP(-\Delta H)e^{-E/RT_{\sigma,s}}}{A\rho C_p RT^2_{\sigma,s}} \frac{1}{1 + \dfrac{d_w z e^{-E/RT_{\sigma,s}}}{Nu_m D_1}} + \frac{Nu_m D_1}{K_1 d_w}\left(1 + \frac{d_w z e^{-E/RT_{\sigma,s}}}{Nu_m D_1}\right) \geq \frac{zC_{\delta,s}EP(-\Delta H)e^{-E/RT_{\sigma,s}}}{A\rho C_p RT^2_{\sigma,s}} \tag{21}$$

Criterion Eq. 15, can be used to obtain kinetic parameters from experimental determination of the surface ignition temperatures, T^*, if we assume that the concentration of species 1 in our control volume prior to ignition is the same as that in the bulk,

$$C_{\delta,s} \approx C_g$$

which is generally valid when under kinetic control.

At ignition the left and righthand sides of inequality of Eq. 17 become equal. This expression can be rearranged to yield

$$\ln\left\{\frac{LPC_{g1}}{\sum_{j=0}^{4} j\alpha_j(T^*)^{j+1} - T^{*2}\left[\frac{\partial(V^2/R_w)}{\partial T_\sigma}\right]_{T^*}}\right\} = \frac{E}{RT^*} + \ln\left[\frac{R}{zE(-\Delta H)}\right] \quad (22)$$

Therefore, a plot of the lefthand side of this expression vs. $1/T^*$ should be linear with slope E/R, if the system behaves in accord with the above assumptions. Kinetic parameters E and z can be obtained frrm the slope and intercept of such a plot. This procedure has been applied by Hiam et al. (1968) for the oxidation of ethane and higher hydrocarbons. In their analysis, however, the role of the V^2/R_w term was not included. The consequences of this omission on derived parameters is discussed below.

Results and Discussion

Surface ignition occurs at one location on the wire, raising the local temperature. As ignition spreads throughout the wire, roughly uniform temperature is attained and the wire resistance increases. The surface ignition event was signaled by the increase in bridge voltage during surface ignition spread. The great increase in catalytic heat generation with ignition resulted in an abrupt reduction in energy input required to maintain a given wire temperature. This is evidenced in Figure 3 for $\phi = 0.50$ methane-air ignition by platinum. Data were recorded at 0.5 s intervals; Figure 3 shows the completion of ignition spread requiring the duration of a few seconds. As described, the experiments were performed by slowly raising the temperature of the two wires until ignition occurred. The low rate of temperature increase ensured small departure of the system from steady state prior to ignition. Experiments were performed at various heating rates; at rapid heating rates inferred ignition temperatures were artificially high since the heating rate exceeded the rate of ignition spread on the wire. As the heating rate was reduced the ignition temperatures approached a limiting value; the runs were performed at a rate giving this value.

The bridge voltage is quite sensitive to ignition: jumps were measured for fuel/air equivalence ratios as lean as $\phi = 0.025$, where negligible energy release is produced. Greater sensitivity could be attained through use of thinner wires; however, due to a reduction in heat transfer with wire diameter, postignition mass transport limited states had higher steady-state temperatures, often high enough to melt the thin platinum wires. Thus, wire diameters were varied in the runs, with thin wires used only for the leanest mixtures where high sensitivity was required.

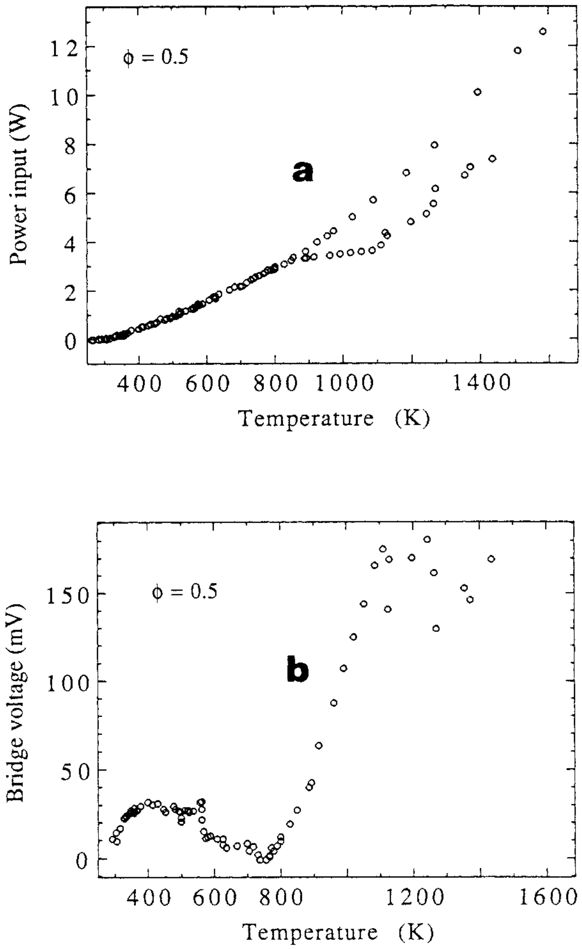

Figure 3. Ignition of $\phi = 0.50$ methane/air by a 250 mm platinum filament.
(a) Power input
(b) Bridge voltage

Figures 3 and 4 show power input and bridge voltage data during typical surface ignition runs. These runs were made for $\phi = 0.50$ methane-air, Figure 3, and $\phi = 1.0$ ethane-air, Figure 4, with a 250 μm platinum wire and a gas flow at 3.4 cm/s velocity. In these and other runs inflammable fuel-air mixtures were diluted with nitrogen to reduce gas phase reactivity and to lower the final flame temperature. Dilution of the total flow was 40% for ethane-air mixtures and 25% for methane-air mixtures. If this dilution were not made, gas phase ignition would follow surface ignition directly, leading to a flame and in most cases melting of the platinum wire. Since N_2 does not interact strongly with platinum this dilution should not affect the dependence of the fuel/oxygen ratio on surface chemistry.

For $\phi = 0.50$ methane-air surface ignition takes place at ~760 K, as shown on the bridge voltage plot, Figure 3a. The wire resistance rapidly increases to a value corresponding to ~1,100 K as ignition spreads throughout the wire, leading to a uniform temperature. From the difference in energy required to maintain a wire temperature in the reactive (ignited) and inert (air) environments, shown in Figure 3b), we can estimate the mass transport limited rate of oxidation. At 1,200 K, this rate is -5×10^{18} molecules/cm^2 s.

In Figure 4 both surface and gas phase ignition are observed for $\phi = 1.0$ ethane/air. At approximately 1,300 K ignition of

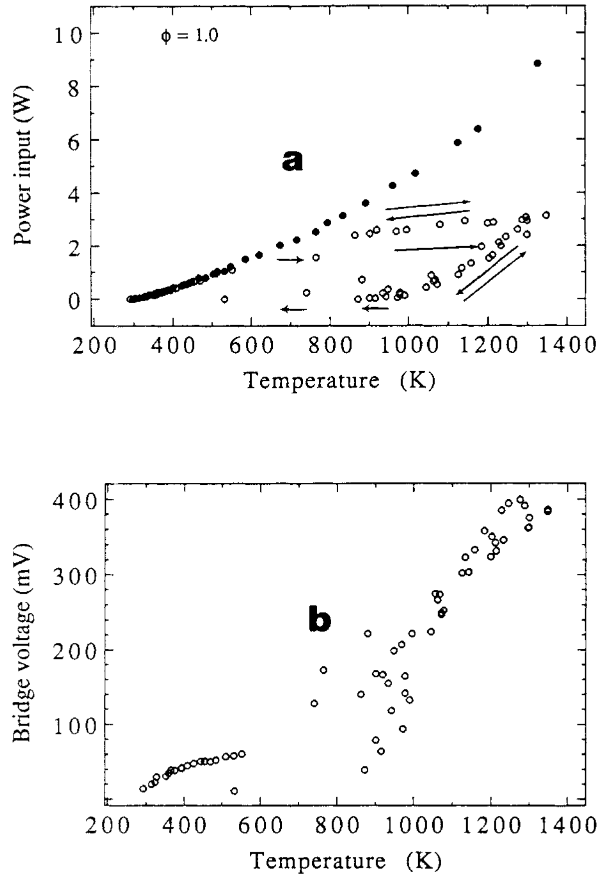

Figure 4. Ignition of $\phi = 1.0$ ethane/air by a 250 mm platinum filament. Arrows indicate sequence in which data recorded

(a) Power input
(b) Bridge voltage

the gas occurs, releasing energy and raising the wire temperature. Subsequent propagation of the ignition away from the wire lowers the wire temperature, as exothermic heat release occurs further and further away. With sufficient nitrogen dilution and/or a flow velocity greater than the flame speed, the propagating flame is extinguished and unreacted gas again reaches the hot wire leading to repeated surface and gas phase ignition. As a result the system oscillates in the range 900 K < T_s < 1,300 K during gas phase ignition/extinction cycles. In addition, the surface ignition/extinction events exhibit hysteresis. Once ignited, the surface reaction was maintained in its mass transport limited state as the external power was reduced to near zero value. The arrows in Figure 4 indicate the sequence in which data were obtained.

Surface ignition temperatures were obtained for a wide variety of fuel/air ratios for ethane and methane fuels to gain some understanding of the surface oxidation kinetics. Under all conditions (down to $\phi = 0.025$) ignition was evidenced below 1,000 K. The data are presented in Figures 5 and 6. For both fuels the ignition temperature rapidly increased below $\phi = 0.50$. For both fuels there was no indication of an abrupt change in behavior at $\phi = 1.0$ as might be expected from the results of Wise and Quinlan (1986), which imply a change in reaction products near $\phi = 1$.

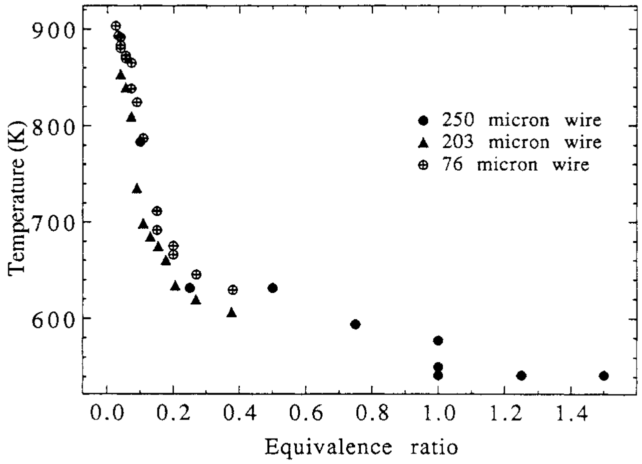

Figure 5. Surface ignition temperatures recorded for ethane-air-nitrogen mixtures.

Subject to the assumptions underlying the development described above in detail, the ignition data should comply with Eq. 22. Thus a plot of

$$\ln\left[\frac{LPC_{g1}}{\sum_{j=0}^{4} j\alpha_i(T^*)^{j+1} - T^{*2}\left[\frac{\partial(V^2/R_w)}{\partial T_s}\right]_{T^*}}\right] \text{vs. } \frac{1}{T^*}$$

should be linear with slope E/R and intercept in $R/zE(-\Delta H)$. Such plots were made for ethane and methane ignition data and are shown in Figures 7 and 8. The V^2/R_w term in the above is significant at approximately 40% of the value of $\Sigma_{j=0}^{4} j\alpha_j(T^*)^{j+1}$. As discussed below, this term was omitted from the analysis of some previous invvstigators where, judging from reaction conditions, it was similarly important.

For ethane-air the data of different wire diameters are described by a line giving an activation energy of 56.9 kJ/mol. Assuming total oxidation to CO_2 and H_2O on the surface, a preexponential of $3.9 \times 10^7\ s^{-1}$ is obtained. The data corresponding to the leanest mixtures tested ($\phi < 0.1$) follow a different line corresponding to an activation energy of 154.7 kJ/mol and a

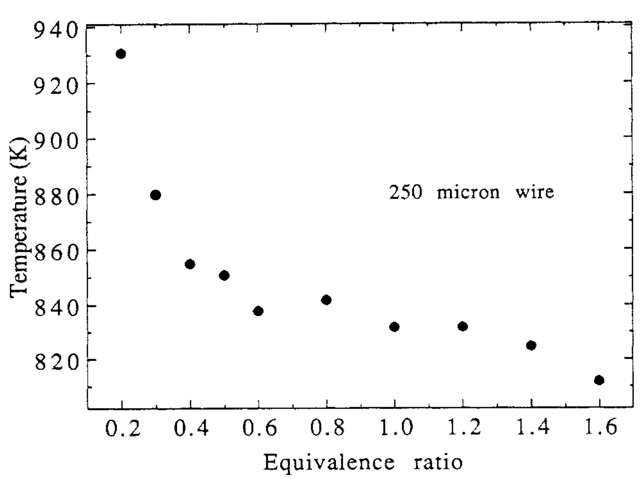

Figure 6. Surface ignition temperatures recorded for methane-air-nitrogen mixtures.

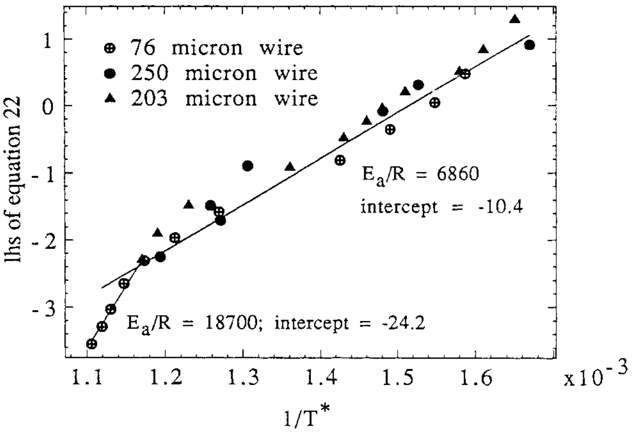

Figure 7. Activation energy plot, Eq. 22, for surface ignition of ethane oxidation.

preexponential of $1.4 \times 10^{13}\ s^{-1}$. The data of these two limiting cases were compared to that obtained by Hiam et al. (1968), in a ln z vs. E plot. Such a plot is often made to highlight the well-known compensation effect, described by Boudart and Djéga-Mariadassou (1984). Interestingly, the data of Hiam et al. fall nearly halfway along the line connecting data from our two limiting cases. It is not known how much the neglect of the V^2/R_w terms in the analysis of the data of Hiam et al. may influence this comparison. In our case, neglect of V^2/R_w shifts the plotted curve to higher y values, changing the y intercept of the plot more than the slope. The change in intercept is -13% and the change in slope several percent.

The data of methane-air contain greater scatter when plotted according to Eq. 22. There are a number of potential causes for this. For methane, there was greater uncertainty in the ignition temperatures in the lean limit—which precluded the investigation of very lean methane-air mixtures. Because of the greater activation energy and exothermicity of the methane oxidation, reaction micro-hot spots are more likely. Another potential cause of nonlinear behavior is related to the change in oxidation products with equivalence ratio as discussed above. Data in Figures 6 and 8 are for lean and rich methane-air mixtures.

Temperature gradients along the platinum wire may also play a larger role in methane surface ignition since both larger diameter wires (250 μm) and higher temperatures were required for ignition than in the majority of the ethane runs. This is discussed below. A linear least-squares fit gives an activation energy 188 kJ/mol for $\phi > 0.4$. This agrees well with the data of Trimm and Lam (1980). A fit of the leanest three data points (around $\phi = 0.4$) yields an activation energy of 105 kJ/mol. Although these data contain large error components, both Hiam et al. ($\phi = 0.4$) has found lean limit activation energies between 84–104 kJ/mol. This suggests a dependence of the surface oxidation rate on the gaseous concentration of oxygen. At a surface temperature of 720 K, Wise and Quinlan (1986) observed different regimes of behavior as a function of the surface oxygen coverage. Under rich conditions ($O_2/CH_4 < 2.0$ by volume) the major gaseous products were CO and H_2; under lean conditions ($O_2/CH_4 > 2.0$) CO_2 and H_2O. The reactivity of adsorbed oxygen was greater when its coverage was low, therefore oxidation/decomposition rates were higher in the rich regime. This is explained by the authors as evidence of two forms of surface oxygen; a highly reactive covalently bonded O(a) and an ionically bonded O^{2-}(a). At the lean equivalent ratio studied, $\phi = 0.4$, the kinetics follow an expression of the form, $r \propto C_{O_2}{}^{1/2}\, C_{CH_4}$, with an activation energy of 85 kJ/mol, which is consistent with our data.

Trimm and Lam (1980) studied methane oxidation on porous and nonporous platinum-coated alumina fiber over a wide range of slightly lean and rich equivalence ratios from 0.9 to 3.0. They also found two regimes of kinetic behavior; however, the regimes were characterized by the surface temperature—below 800 K an activation energy of ~175 kJ/mol was measured, above 800 K, ~80 kJ/mol, with an oxygen reaction order between 0.75 and 1.0. The temperature dependence is likely the result of external mass transport intrusion on the reaction rate since we found catalytic ignition temperatures for methane-air to fall between 800 and 850 K for similar Nu_m, ($h_m d_w/D$). Similar results obtained for porous and nonporous fibers rule out the influence of internal pore diffusion. The data of Trimm and Lam for $T <$ 800 K correspond with our measured methane oxidation rates for $\phi > 0.1$ with an activation energy measured in this study of 188 kJ/mol, compared to 175 kJ/mol measured by Trimm and Lam.

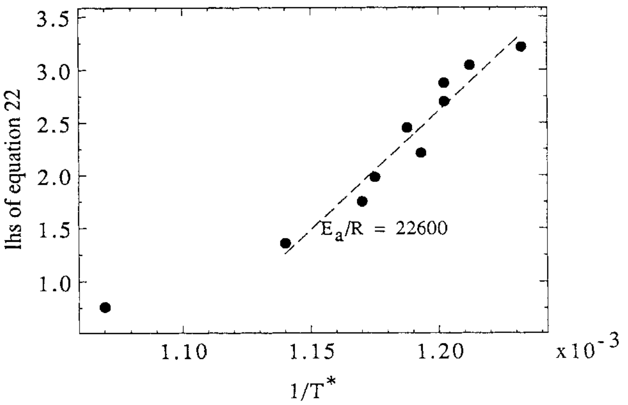

Figure 8. Activation energy plot, Eq. 22, for surface ignition of ethane oxidation.

Effect of nonuniform surface temperature

In the above analysis it was assumed that the wire temperature was uniform throughout its length. In reality the wire temperature will vary from near room temperature at its ends—connected to high heat capacity brass terminals—to a maximum temperature at its center point. Hinze (1959) and Edwards et al. (1973) have analyzed the temperature distribution along electrically heated wires placed in a uniform flow stream. Assuming conduction in the wire to be the only mode of energy loss, the average temperature, T_w, and center point temperature, T_{cp}, of the wire are related in the following way,

$$\frac{T_{cp} - T_o}{T_w - T_o} = \frac{\lambda \cosh \lambda - \lambda}{\lambda \cosh \lambda - \sinh \lambda} \tag{23}$$

where

$$\lambda = \frac{L\{i^2 R(T_o)\gamma[R(T_o) - \eta R(T_w)]\}^{1/2}}{d_w\{Lk_w\pi[R(T_w) - R(T_o)]\}^{1/2}} \tag{24}$$

and the fractional end loss is defined

$$\eta = \frac{\pi k_w d_w^2 \lambda \tanh[\lambda(T_w - T_o)]}{V^2/R_w(T_w)L\left(1 - \dfrac{\tanh \lambda}{\lambda}\right)} \tag{25}$$

These relationships have been derived for the following boundary conditions: $T_w = T_o$ at $x = 0$ and $x = L$. It should be noted that the above relations assume that convective and radiative heat transfer are negligible.

Edwards et al. (1973) have reported excellent agreement between their experimental spatially resolved wire temperature measurements and these theoretical predictions under conditions similar to those in our experiments. Hinze (1959) recommends that λ should be greater than 5 for a "reasonably uniform surface temperature distribution."

The average wire temperature, determined by the total resistance of the wire, can be compared to the maximum wire temperature to determine the possible role of temperature gradients on our surface ignition experiments. Test calculations were performed for 3.5 cm long, 76 and 250 μm dia. wires, utilizing experimental wire currents and resistances. For the 76 μm wires the $\lambda = 5$ condition is satisfied and the maximum surface temperature is 50–100 K higher than the average. The surface temperature nonuniformity becomes more pronounced for the larger 250 μm dia. wire, with the maximum ~200 K higher than average.

Ignition should occur first at the highest temperature location. Thus, we are underestimating the "true," local ignition temperature by reporting the mean, resistance-averaged temperature. However, since radiative and convective heat losses cool the higher temperature regions of the wire to a greater extent than the cooler regions, the above analysis overestimates temperature nonuniformities. Our energy loss curves as a function of wire diameter are not consistent with losses due solely to conduction. Therefore, the effect of surface temperature gradients on parameter estimation is likely not as large as other experimental sources of uncertainty. This is suggested by Figure 7, in which ignition data obtained with 76, 203, and 250 μm dia. platinum wires are described by one linear fit, although surface temperature gradients are different for these wires.

Gas-phase ignition revisited

Utilizing the surface ignition apparatus described above decoupled surface and gas phase ignition experiments were performed to further probe the phenomena near $\phi = 1.0$. These experiments were made with $Re < 1$ flows. Recognizing the potential influence of transient heating of the wire, the final, mass transport limited operating temperature of the wire was reduced by diluting the mechane-air mixtures with sufficient nitrogen to comprise 25% of the total gas. In this way the surface and gas phase ignition events were separated, ensuring mass transport limited conditions on the catalyst wire during interactions leading to gas phase ignition. Gas phase ignition was recorded by monitoring the drop in bridge voltage (resulting from a lowering in the wire resistance-temperature), as described above. The results are shown in Figure 9 with error bars. The relative uncertainty (precision) in recorded gas phase ignition temperatures was fairly high, ±50 K, resulting from nonuniform wire temperature and variable wire heating rate. The data show no sharp maximum near the stoichiometric condition. Therefore, it is likely that the sharp maximum in wire temperature required for gas phase ignition at $\phi = 1.0$ for methane in air is largely an artifact caused by gas phase ignition during the transient heating of the actively heated wire during the transition to mass transfer limited surface oxidation. This effect is exacerbated by the high surface temperatures required for ignition of methane.

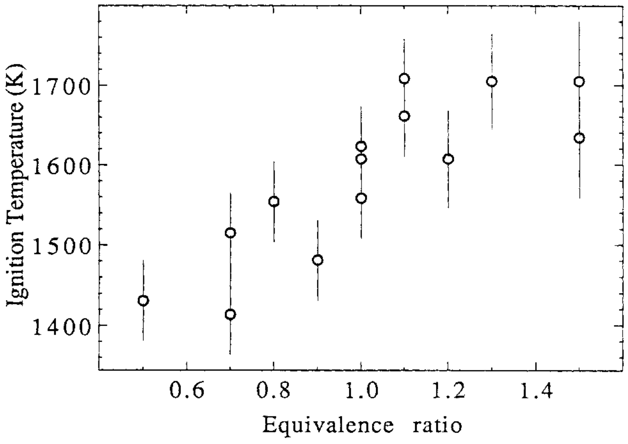

Figure 9. Wire surface temperature at gas phase ignition of methane-air-nitrogen mixtures in surface ignition apparatus.

Conclusions

Fine wire experiments were used to determine kinetic rate data for ethane and methane oxidation on platinum at high temperatures for use in numerical models of gas phase ignition experiments. Our data compare well with those of previous investigators and show different mechanisms for methane and ethane oxidation on platinum at ultralean conditions.

The gas phase ignition of fuel-air mixtures by heated catalytically active surfaces was also studied and was found to be a complex process involving the dynamics of both surface and gas phase processes. By carefully monitoring the surface ignition process and adjusting the experimental variables (heating rate, velocity, dilution, and wire diameter) we were able to decouple surface and gas phase ignition events. Experiments performed in this way did not result in a sharp peak in gas phase ignition temperature required for stoichiometric methane-air mixtures. This suggests that transient heating plays a role in producing the sharp peak in ignition temperature at $\phi = 1.0$ reported by Coward and Guest and others for ignition of natural gas-air mixtures over platinum and palladium surfaces. Greater surface temperatures for ignition over catalytically active surfaces were expected for some flammable equivalence ratios because mass transfer limited surface oxidation of the fuel creates a starvation of the limiting reactant near the surface, suppressing gas phase reactivity with respect to a noncatalytic heated surface. However, a platinum catalyst can also promote the production of oxidizing radicals accelerating gas phase ignition (Pfefferle and Pfefferle, 1987).

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Notation

$a_{11}, a_{12}, a_{21}, a_{22}$ = coefficients in linearized conservation equations; units: a_{11}, s^{-1}; a_{12}, mol/s · cm^3 · K; a_{21}, K · cm^3/mol · s; a_{22}, s^{-1}
A = cross-sectional area of wire, cm^2
c = departure of species 1 (rate limiting species) from steady state value, mol/cm^3
C = bulk concentration of limiting reactant, mol/cm^3
C_{gi} = bulk concentration of species i, mol/cm^3
$C_{\delta,i}$ = gas phase concentration of species i adjacent to surface, mol/cm^3
$C_{\delta,s}$ = steady state concentration of limiting reactant, mol/cm^3
C_σ = surface concentration vector, mol/cm^2
C_p = heat capacity of catalyst, cal/g · K
D_i = diffusivity of species i in the mixture, cm^2/s
d_w = diameter of wire, cm
E = activation energy of catalytic reaction, cal/mol.
$-\Delta H$ = enthalpy of surface reaction, cal/mol
i = current through catalyst wire, amps
K_i = equilibrium constant for the adsorption of species i
k = thermal conductivity of air, cal/cm · K
k_{eff} = effective, first order rate constant of surface reaction, cm/s
k_w = thermal conductivity of wire, W/cm · K
L = length of wire, cm
Nu_h = Nusselt number for heat transfer
Nu_m = Nusselt number for mass transfer (Sherwood number)
P = perimeter of wire, cm
Pr = Prandtl number
q''_{rad} = radiative rate of heart loss per unit area, cal/cm^2 · s
r = rate of catalytic surface reaction, mol/cm^2 · s
R = gas constant, cal/mol · K
Ra = Rayleigh number
Re = Reynolds number
$R(T)$ = resistance of wire at temperature T, ohm
R_w = resistance of wire, ohms
S = total number of active catalytic sites per unit area, cm^{-2}
t = departure of catalyst surface temperature from a steady-state value, K
T, T_σ = surface temperature of catalyst, K
T_g = temperature of bulk gas, 300 K
$T_{\sigma,s}$ = steady-state surface temperature of catalyst, K
V = electrical potential across catalyst wire, volts
z = preexponential factor for power law surface kinetic rate constant, $(cm/s)(\mathrm{cm}^3/\mathrm{mol})^{n-1}$

Greek letters

α_i = coefficients of polynomial expression for heat removal rate, cal/s(K)^i or W/(K)^i
δ = subscript, gas phase concentration adjacent to surface
$\gamma_{1,2}$ = roots of characteristic equation, s^{-1}
ϕ = equivalence ratio
ν_i = stoichiometric coefficient of species i in surface reaction
ρ = density of catalyst wire, g/cm^3
σ = subscript, surface-related variable

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