The critical condition for catalytic ignition. H₂/O₂ on Pt

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The Frank-Kamenetskii condition for catalytic ignition (the sudden transition from a kinetically to a mass transport controlled, exothermic catalytic reaction), is explored experimentally and by simulations for the H₂+ O₂→H₂O reaction on Pt. At ignition the temperature derivatives of the dissipated chemical power and the heat loss, respectively, are equal [1]. This condition is verified by measurements of the pre-ignition kinetics and calculations taking into account kinetics, heat, and mass transport. The ignition temperature is determined by a competition between hydrogen site blocking on the surface and hydrogen desorption, which makes the ignition temperature increase with increasing H₂/O₂ ratio.

1. Introduction

Catalytic ignition, as defined here and in ref. [1], is a critical phenomenon where a surface catalyzed reaction undergoes a transient change from one stable, stationary state to another. More specifically the system changes from a pre-ignition state, controlled primarily by surface reaction kinetics, to a post-ignition state primarily governed by mass transport of reactants to the catalyst. The catalytic ignition condition can be qualitatively understood as follows [1].

Consider a catalytically active, solid wire in a gas of particles A and B which can react exothermically to form products AB. The reaction, which can occur only on the surface of the catalyst, is assumed to be thermally activated. At sufficiently low temperature the reaction rate, and thus the heat release, is low. When the temperature is raised by external heating, the rate and heat generation will increase successively, typically as \( \exp(-E/kT) \), while the heat loss to the environment has a weaker temperature dependence of the form \( (T-T₀)^β \) \( (β≈1) \), when radiative losses are negligible \( (E) \) is the overall activation energy for the reaction, \( k \) is the Boltzmann constant, \( T \) is the surface temperature and \( T₀ \) is a reference temperature of e.g. the surrounding gas. It is apparent that at some value of \( T \) the system will not be stable and instead self-accelerate in temperature. We call this critical temperature the ignition temperature, \( T_i \). This ignition condition was discussed already by Frank-Kamenetskii [1] and can be written

\[
γ = \frac{dQ_c/dT}{dQ_e/dT} = 1,
\]

where \( Q_c \) and \( Q_e \) are the temperature-dependent chemical power generation and heat losses, respectively, at the catalyst surface. The system contains three main ingredients: (i) the surface kinetics by which reactants are converted to products, which then desorb into the gas phase, (ii) the energy balance describing how the externally and chemically generated power \( (Q_{ext} \ and Q_c \ respectively) \) in steady-state are balanced by the heat losses, \( Q_l \ (Q_{ext} + Q_c = Q_l) \), and (iii) the mass transport of reactants in the gas phase by diffusion to the catalyst.

In the pre-ignition regime, \( γ < 1 \), the system is normally stable and stationary (unless conditions for kinetic phase transitions are fulfilled [2]). When the condition in eq. (1) is reached, a small perturbation (e.g. an infinitesimal fluctuation in either of the \( Q \) terms) may make \( γ > 1 \) and ignition will then occur.

Recent work, pioneered by Ertl and co-workers [2], on oscillations driven by surface kinetics, has stimulated our interest in catalytic ignition since it may be central in other types of oscillatory phenomen...
ena involving both kinetics, heat and mass transport [3,4].

The phenomenon is of inherent scientific interest, but also of technological importance. This has motivated many experimental studies of ignition, especially with catalytically active wires, and associated theoretical analyses [5–8]. The latter have, however, with a few exceptions [3,9] not treated the surface kinetics explicitly.

In a recent paper [3] we presented new data and a theoretical model for the ignition temperature, $T_i$, for the $\text{H}_2/\text{O}_2$ reaction on Pt, as a function of $\text{H}_2/\text{O}_2$ mixing ratio. The calculations were based on a combination of explicit kinetics and diffusive mass and heat transport, using the steady-state approximation. In the present work the focus is instead primarily on pre-ignition regime and how the ignition condition (eq. (1)) is approached. Specifically we explore experimentally and by associated theoretical modeling, the Frank-Kamenetskii condition for ignition, using the catalytic oxidation of hydrogen on Pt as our model system. We also discuss how the special kinetic features of this particular system affect the approach to catalytic ignition. Finally some improvements of the previous model [3] are described, that produces better agreement between measured and calculated ignition temperatures versus $\text{H}_2/\text{O}_2$ mixing ratio.

2. Experimental

The experiments were performed with a (non-flammable) $\text{H}_2/\text{O}_2/N_2$ gas mixture at 760 Torr total pressure. $N_2$ served as a carrier gas, and $\text{H}_2/\text{O}_2$ constituted $\approx 6\%$ of the gas mixture. Measurements were performed at different relative $\text{H}_2$ concentrations, $\alpha = p_{\text{H}_2}/(p_{\text{H}_2} + p_{\text{O}_2})$. The experimental setup is relatively simple, and consists of a $\phi = 0.127 \text{ mm}$ Pt wire, which can be heated by an electric current. It is positioned diametrically inside a quartz tube of 19 mm inner diameter. The Pt-wire catalyst forms a Pt thermometer whose temperature is measured via its $T$-dependent resistivity. The high-purity gas mixture was slowly fed through the system $(w \approx 0.9 \text{ cm/s})$. This flow is sufficiently low, that the main heat loss channel is heat diffusion (which was controlled by measuring the heat loss as a function of flow velocity). Temperature gradients along the wire are small.

3. Experimental results

In the experiment the temperature of the wire was slowly raised in small steps. After each step the steady-state temperature was measured. From these data points the chemical power was extracted, using the calibrated heat loss function. Eventually the critical condition corresponding to eq. (1) was reached (except at high $\alpha$ values where ignition did not occur, see inset in fig. 2b). At this temperature, $T_i$, the temperature rose spontaneously without additional external heating, until the mass-transport-controlled, steady state was established. In the inset of fig. 1 two such ignition curves are shown. The overshoots in the $T(t)$ curves, shortly after the ignition, are due to relatively larger reactant concentrations close to the wire at this moment compared to later times. The main result of fig. 1 is $T_i$, as a function of the relative $\text{H}_2$ concentration, $\alpha$. A noticeable result is the monotonic increase in $T_i$ as the $\text{H}_2$ fraction in the $\text{H}_2/\text{O}_2$ mixture increases. This is a consequence of self poisoning of the catalytic reaction by accumulation of hydrogen atoms on the Pt surface as discussed in ref. [3]. These $T_i$ data will be further discussed below.

![Fig. 1. Experimental (filled symbols) and calculated (full curve) ignition temperature as a function of $\alpha = p_{\text{H}_2}/(p_{\text{H}_2} + p_{\text{O}_2})$. The inset shows two of the ignition curves, used to determine the ignition temperatures. The horizontal error bars derive from the limited accuracy in the $\alpha$ measurements. Vertical error bars are of the same size as the experimental points. The data scatter is predominantly due to variations in the catalyst status.](image-url)
Referring to section 1 and eq. (1) it is of obvious interest to explore how the ignition temperatures displayed in fig. 1 are approached and what kinetic and other potential factors determine the ignition condition. For example, ignition will not necessarily take place, as demonstrated by the behavior at large H₂ excess, $\alpha > 0.75$, where no ignition was observed experimentally (see discussion below).

Fig. 2a shows the measured rate versus tempera-
ture in the pre-ignition regime for two $\alpha$ values, together with the corresponding model calculations (full curves). The kinetics show typical Arrhenius-like behavior (inset in fig. 2a), but with different apparent activation energies at different $\alpha$ values (e.g. for $\alpha = 0.2$ and $\alpha = 0.5$ the apparent activation energies are $10.9 \pm 0.2$ and $8.2 \pm 0.4$ kcal/mol, respectively). The latter is not surprising since the kinetics consist of several consecutive steps [10] with different relative weights at different $\alpha$, $T$ conditions. The experimental error bars are primarily due to uncertainties in the procedure to obtain the chemical power. The latter involves extracting a small difference between two comparably large numbers, namely the external input powers with and without reaction, respectively.

A convenient way to experimentally explore the ignition condition [1], i.e. $\gamma = 1$ (eq. (1)), is to plot the experimental $\gamma_e$ versus $T$. The $\gamma_e$ values should then approach, but never exceed, unity. This behavior is in fact what fig. 2b demonstrates. The $\gamma_e$ values approach unity but seldom exceed 0.9. The fact that values above 0.9 are not measured is attributed to the experimental uncertainties in defining $T_i$ and uncertainties in the measured $Q_e$ and $Q_i$ curves (see discussion in ref. [3]).

4. Simulations and discussion

The mathematical model used for the calculations, describes the three essential ingredients/processes relevant for the ignition and the approach to ignition; namely surface kinetics, mass transport and heat transport/energy balance, respectively. For the surface kinetics we use a somewhat simplified version of a model [10], originally developed to describe steady-state kinetics for H₂ + O₂ on Pt, at lower pressures and higher temperatures than considered here:

$$\frac{d \Theta_i}{dt} = k_i(1 - \Theta_i)^{x_i - k_i \Theta_i^2 - k_i \Theta_1 \Theta_2,}$$

$$i = 1, 2,$$

where $\Theta_1$ and $\Theta_2$ are the relative surface coverages of hydrogen and oxygen atoms (dissociative adsorption is assumed, for details see ref. [10]) and $\Theta_1 + \Theta_2 = \Theta$. $k_i$ are the adsorption rate constants.
(proportional to the product of the impingement rate and the sticking probability). $k_i^a$ is the rate constant for hydrogen desorption, while $k_i^b$ is set to zero because the temperature is low enough that oxygen desorption can be neglected \[10\]. The last term of eq. 2 represents consumption of H and O by the water formation reaction. In principle this term should be replaced by three terms \[10\], describing the consecutive OH and H$_2$O formation steps and H$_2$O desorption. For the present purpose it is sufficient with one term, provided a representative choice of the magnitude of $k_i^b$ is made. Mass conservation requires that $k_i^b = 2k_i^a$. The absolute value of $k_i^a$ is given by $k_i^a = v \exp(-E_i^a/k_B T)$ and table 1. The value of $E_i^a$ was chosen slightly higher than in our previous work on OH formation, but well within the range of reported activation energies for OH formation (see discussion in ref. \[10\]). This value gives a somewhat better overall fit to the data than lower values, but the choice is not critical (see ref. \[31\]).

In comparison with ref. \[3\] we now treat the water formation step explicitly (third term on the right-hand side of eq. (2)), which (i) means that we have relaxed the condition in ref. \[31\] that the reaction is so fast that only adsorption and desorption steps need to be considered, and (ii) allows us to include an activation energy for water formation that depends on surface coverage (the latter is quite likely, as shortly discussed in e.g. ref. \[14\]).

For heat transport/energy balance and mass transport, respectively, equations assuming cylindrical symmetry around the catalyst wire were used,

\[
C \frac{dT}{dt} = Q_e + Q_{es} - Q_t,
\]

\[
\frac{dn_i(r, t)}{dt} = \mathcal{D}_i \left( \frac{dn_i^2(r, t)}{dr^2} + \frac{1}{r} \frac{dn_i(r, t)}{dr} \right),
\]

\(i=1, 2\).

The heat loss function $Q_t$ in eq. (3) describes the cooling of the wire by heat diffusion. Experimental calibration yielded the functional form

\[
Q_t = 0.51 (T - T_0)^{1.14} \text{mW},
\]

with $T_0$ equal to the ambient temperature.

In eq. (4) $n_i$ are the reactant concentrations as functions of radial distance from the wire. These equations were solved with the boundary condition that the reactant concentrations (H$_2$ and O$_2$) at the reactor inlet were the same as in the unreacted gas mixture.

The whole set of eqs. (2)–(4) were solved numerically with suitable time steps to warrant convergence. Eqs. (3) and (4) were solved by the finite element method. The parameters used to calculate the curves in figs. 1 and 2 are given in table 1. For motivations of these choices see discussions in refs. \[3,10,14\]. The agreement with experimental data is here better than in ref. \[3\] primarily since the loss function (eq. (5)) used in the model now was obtained experimentally (in ref. \[3\] a linear loss function was used). Other contributing factors such as the modified kinetics and influences of mass gradients will be discussed in a forthcoming publication \[14\]. The main results are as follows.

Considering the pre-ignition kinetics (fig. 2a), i.e. the reaction rate versus $T$ (or equivalently $Q_e$ versus $T$), the calculations give a reasonable account of the data, especially of the functional form close to ignition. Fig. 2b shows the experimental and calculated $\gamma$ versus $T$. The experimental $\gamma_e$ values were obtained by using the results of fig. 2a and eq. (5). Again the calculations agree well with the experiment. The calculated curves intersect the $\gamma=1$ line.

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Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Ref.</th>
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<tr>
<td>$S_{O_2}(0)^a$</td>
<td>0.02</td>
<td>[10]</td>
</tr>
<tr>
<td>$S_{H_2}(0)^a$</td>
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<td>[10]</td>
</tr>
<tr>
<td>$\nu$</td>
<td>$10^{13}$ s$^{-1}$</td>
<td>[10]</td>
</tr>
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<td>$x_2$</td>
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<td>[3]</td>
</tr>
<tr>
<td>$x_1$</td>
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<td>[3]</td>
</tr>
<tr>
<td>$D_{H_2}$</td>
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<td>[10]</td>
</tr>
<tr>
<td>$D_{O_2}$</td>
<td>0.18 cm$^2$/s</td>
<td>[10]</td>
</tr>
<tr>
<td>$E_i^a$</td>
<td>9.2 kcal/mol</td>
<td>see [10] and references therein</td>
</tr>
</tbody>
</table>

$E_i^{H_2}(0)^b$ | 19 kcal/mol | [11-13] |

$A^b$ | 8 kcal/mol |

$\Delta H$ | 58 kcal/mol |

$r_s$ | 0.063 mm |

$P_{H_2} + P_{O_2}$ | 45 Torr |

$P_{tot}$ | 760 Torr |

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$^a$ $S_{i}(0)$ are the zero coverage sticking coefficients.

$^b$ The coverage dependence is given by $E_i^{H_2}(\Theta) = E_i^{H_2}(0) - \Delta \Theta$, where the value of $E_i^{H_2}(0)$ is an average over several literature values.
exactly at the corresponding ignition temperatures shown in fig. 1. The ignition temperature versus $\alpha$ (fig. 1) is extremely well reproduced.

Fig. 2b also shows (in the inset) a calculation for $\alpha=0.82$, where ignition was not observed experimentally. The model explains the absence of ignition; the condition $\gamma=1$ is here never reached. The reason is a concerted effect of increasing hydrogen poisoning with increasing $\alpha$ and influence of gradients in the $O_2$ concentration (i.e. $O_2$ mass transport limitations), causing the system to make a smooth, continuous transformation from kinetic to mass transport control, as the temperature increases. The system thus does not self-accelerate or ignite in this case. Experimentally the ignition case is recognized by the spontaneous temperature rise that occurs at the critical temperature $T_i$, while the non-ignition case is characterized by a smooth change in temperature at all temperatures upon incremental increases of the external heating.

5. Summary

We have gained considerable insight into how the catalytic ignition condition, eq. (1), is approached, and how the particular features of the $H_2+O_2$ on Pt system come into play in determining the critical condition for ignition. The condition expressed by eq. (1) correlates well with the experimental results. Furthermore, the increase of $T_i$ with $\alpha$ is a consequence of a continuous decrease (at a given temperature) of $dQ_i/dT$ with increasing $\alpha$, which in turn has its origin in a successively increasing hydrogen poisoning as $\alpha$ increases, which must be compensated by an increased hydrogen desorption rate, for ignition to occur. The hydrogen poisoning is primarily a consequence of an asymmetry in the coverage dependencies ($x_2>x_1$ in eq. (3), see table 1) of the hydrogen and oxygen adsorption rates [3,10].

At sufficiently large $\alpha$, gradients in $O_2$ in the gas phase become important and prevent the system from reaching the ignition condition $\gamma=1$.

A more detailed account of these data, of calculations of the transient ignition curves (inset of fig. 1), and of stationary states after ignition at different $\alpha$, will be presented in a forthcoming publication [14].

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References