DETERMINATION OF ADSORPTION AND DESORPTION PARAMETERS FROM HETEROGENEOUS IGNITION TEMPERATURE MEASUREMENTS

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Abstract

In heterogeneous combustion, reaction of fuel and oxygen occurs on a catalyst surface. The surface of a cold catalyst is covered with the more effectively adsorbing species; when the temperature is increased, this species is desorbed, and the rates of adsorption and desorption determine the ignition temperature. Based on the equations for the heat balance, expressions were derived for the calculation of ignition temperature from the parameters of the experimental setup and the physical parameters of adsorption and desorption. These physical parameters are the preexponential factor A_D and activation energy E_D of desorption, the ratio of zero coverage sticking coefficients, and the ratio of adsorption orders of fuel and oxygen. Several published experimental ignition temperature measurements were reanalysed to obtain adsorption desorption parameters for CO, H_2, CH_4, C_2H_4, and C_3H_6 on polycrystalline platinum catalyst. The following parameters were determined via nonlinear least-squares fitting: activation energies of desorption: $E_D(H_2/Pt) = 43.3 \pm 5.2$ kJ/mol, $E_D(CO/Pt) = 107.2 \pm 12.7$ kJ/mol, $E_D(O_2/Pt) = 190 \pm 34$ kJ/mol, $E_D(C_2H_4/Pt) = 136 \pm 21$ kJ/mol, $E_D(C_3H_6/Pt) = 161 \pm 53$ kJ/mol; ratio of sticking coefficients: $S_{H_2,0}/S_{O_2,0} = 36.7 \pm 9.6$, $S_{CO,0}/S_{O_2,0} = 41.2 \pm 8.5$, $S_{O_2,0}/S_{CH_4,0} = 5.9 \pm 0.3$, $S_{C_2H_4,0}/S_{O_2,0} = 15.6 \pm 1.9$, $S_{C_3H_6,0}/S_{O_2,0} = 11.9 \pm 1.7$. Error limits refer to a confidence level of 0.95. Experimental ignition temperatures could be reproduced assuming second order adsorption of CO, H_2, O_2, CH_4, C_2H_4, and C_3H_6 on polycrystalline platinum. These reaction orders have been debated in the literature.

Introduction

When a bare catalyst is exposed to a mixture of fuel and oxygen, the surface gets covered with the more effectively adsorbing species. Depending on conditions, either the fuel or the oxygen has initially a higher coverage. If the fuel has a higher initial coverage, the oxygen atoms on the surface will be soon consumed in the surface reaction. After the fast desorption of the product, the vacant sites will be occupied mainly by the fuel, and the small amount of adsorbed oxygen will also be consumed. Therefore, after a few such steps, the surface becomes almost fully covered by the fuel. When the ratio of fuel in the gas mixture is increased, the reactivity of the mixture decreases and consequently the heterogeneous ignition happens only at higher temperature. This means that increasing the fuel/oxygen ratio in the gas mixture, the ignition temperature increases. Such behaviour has been observed in the following systems: $H_2/O_2/Pt$ [1], $CO/O_2/Pt$ [1], ethene/O_2/Pt [1], propene/O_2/Pt [1, 2, 3], and $NH_3/O_2/Pt$ [4]. In the opposite case, the surface is almost completely covered with oxygen atoms and the increasing fuel/oxygen ratio decreases the ignition temperature. Such systems are the $CH_4/O_2/Pt$ [4, 5, 6], ethane/O_2/Pt [5, 7], propane/O_2/Pt [1, 4, 6, 8], and butane/O_2/Pt [1, 8] systems.

Recently we published [9] a new method for the evaluation of heterogeneous ignition temperature measurements using an analytical model, which is based on the heat balance and the Frank-Kamenetskii condition. It was assumed there that the rate limiting step is the desorption of the dominant species from the surface of the catalyst. Equations were deduced to relate the ignition temperature to the gas composition, the experimental parameters and the physical parameters of adsorption and desorption. These equations can be used to predict the ignition temperature as a function of the composition of the gas, if the physical parameters of adsorption and desorption and the parameters of the experimental setup are known. On the other hand, the equations can be applied to evaluate heterogeneous ignition temperature measurements and to obtain unknown physical parameters via nonlinear least-squares fitting.
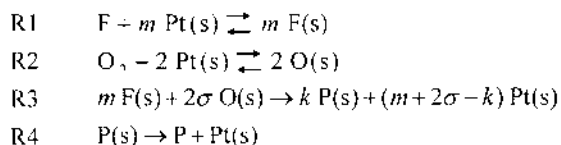
In this paper, the derivation of these equations are briefly reviewed, the results obtained for $CO/O_2/Pt$, $H_2/O_2/Pt$ and $CH_4/O_2/Pt$ systems are summarized, and the same equations are used for the determination of the adsorption and desorption parameters of ethene and propene. For a complete discussion of the derivation of the equations and further details on the CO. H_2 and CH_4 systems please refer to the general article [9].

Analytical expressions for the calculation of ignition temperature

Reaction of fuel and oxygen gases on a catalytic surface can be described by the following overall reaction:

$$F + \sigma\, O_2 \rightarrow P \tag{1}$$

The detailed elementary mechanism can be very complicated, but has to contain the competitive adsorption–desorption equilibrium of fuel and oxygen, the reaction of adsorbed species on the surface and the desorption of reaction products [10]:

R1 $F + m\,Pt(s) \rightleftarrows m\,F(s)$

R2 $O_2 + 2\,Pt(s) \rightleftarrows 2\,O(s)$

R3 $m\,F(s) + 2\sigma\,O(s) \rightarrow k\,P(s) + (m + 2\sigma - k)\,Pt(s)$

R4 $P(s) \rightarrow P + Pt(s)$

Symbols F, O_2 and P denote the fuel, oxygen molecule and product species, respectively, in the gas phase; F(s), O(s) and P(s) denote the fuel, oxygen atom and product species on the surface, respectively and Pt(s) denotes a vacant site. Adsorption of each fuel species requires m vacant sites. Note that step R3 can be either an elementary reaction on the surface, or an overall reaction that incorporates all surface reactions.

In catalytic ignition experiments, the catalyst is usually a Pt plate or Pt wire. A frequently used experimental setup is when a catalytic wire is placed in a cross-stream gas flow [1, 11, 12]. In such experiments, temperature of the catalyst is increased to just below the ignition temperature. Having reached a stationary state, a small extra heating will ignite the system and the temperature vs. time curve is recorded until a new stationary state is achieved. Due to the exothermic chemical reaction and the external heating, temperature T of the surface of the catalyst is always higher than temperature T_∞ of the inlet gas flow far from the catalyst. Temperature T is determined by the heat balance, that is heat production by electric heating and chemical reactions is equal to heat loss. Due to the relatively low temperature, conductive and radiative heat transport can be neglected and heat loss is mainly due to cooling of the catalyst by the gas flow, called convective heat transport. According to the theory of heat transfer [13], convective heat loss depends linearly on the difference of temperature T of the

surface and temperature T_∞ of the gas far from the surface and is proportional to the ratio of the heat conductivity λ of the gas and the characteristic thermal length L_c:

$$\omega \Delta_r H + Q_2 = \frac{\lambda}{L_c}(T - T_\infty) \tag{2}$$

Here $\Delta_r H$ is the enthalpy of the overall reaction, ω is the rate of the overall reaction, and Q_2 is the rate of heat production due to electric heating. The characteristic thermal length L_c can be calculated from the flow geometry [13]. For stagnation point flow configurations,

$$L_c = 2 \times 10^{-2} \sqrt{v / a} \tag{3}$$

where v is the kinematic viscosity of the gas at temperature T_∞ and a is the velocity gradient of the gas flow. Units of L_c, v and a are m, m^2 s^{-1} and s^{-1}, respectively. If a wire of diameter d is placed perpendicularly in a flow of velocity u, the characteristic thermal length is

$$L_c = \frac{d}{0.891 \times 10^2 Re^{0.33}} \tag{4}$$

where Re is the dimensionless Reynolds number ($Re = ud / v$).

Before ignition, the surface temperature is determined by the balance of the electric heating, the heat production of the surface reactions and the heat loss; the heat production of the electric heating is more significant than that of the chemical reactions. Any increase in the surface temperature requires additional electric heating. At the ignition temperature, infinitesimal increase in the external heating results in a large change of surface temperature. In the moment of ignition, the temperature increases spontaneously due to the chemical reactions, without additional heating. According to the Frank-Kamenetskii condition [14], differentiating equation (2) with respect to the temperature results in an expression for the condition of ignition:

$$\frac{\partial \omega}{\partial T} \Delta_r H = \frac{\lambda}{L_c} \tag{5}$$

In this equation, λ and L_c can be calculated from the conditions of the experiment and $\Delta_r H$ is a well-known value. Rate of overall reaction ω can be obtained from the differential equations for the surface coverage of species. However, due to the stoichiometry of reaction steps, the overall reaction rate and the time derivatives of surface coverage of species are not independent. The following equations relate the rate of overall reaction ω to the rate coefficients of adsorption and desorption of the fuel and oxygen ($k_{F,A}$, $k_{F,D}$, $k_{O,A}$, $k_{O,D}$), the surface coverage of fuel, oxygen and vacant sites (θ_F, θ_O, θ_v), and the reaction order of adsorption and desorption of the fuel and oxygen ($n_{F,A}$, $n_{F,D}$, $n_{O,A}$, $n_{O,D}$):

$$\frac{\omega}{\Gamma} = k_{F,A} \theta_v^{n_{F,A}} - k_{F,D} \theta_F^{n_{F,D}} \tag{6}$$

$$\frac{\omega}{\Gamma} = \frac{1}{\sigma}\left(k_{O,A} \theta_v^{n_{O,A}} - k_{O,D} \theta_O^{n_{O,D}}\right) \tag{7}$$

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In these equations Γ is the density of active sites on the surface of the catalyst, which is $\Gamma = 2.707 \times 10^{-5}$ mol m^{-2} [15] in the case of Pt catalyst.

Rate coefficient of adsorption of species i at zero surface coverage is equal to the number of species hitting the surface multiplied by the zero-coverage sticking coefficient $S_{i,0}$ [16]:

$$k_{i,A} = \frac{S_{i,0} p_i}{\Gamma \sqrt{2\pi W_i RT}} \tag{8}$$

where W_i and p_i are the molar mass and the partial pressure of species i in the gas phase, respectively. Partial pressures can be expressed as $p_i = pX_i$, where p is the total pressure and X_i is the mole fraction of species i.

The rate coefficient of desorption can described by an Arrhenius expression:

$$k_{i,D} = A_{i,D} \exp\left(-E_{i,D} / RT\right) \tag{9}$$

Note that in equation (9), preexponential factor $A_{i,D}$ was expressed with surface coverages and not with surface concentrations.

Initial fuel coverage. If initially the surface is almost completely covered with fuel ($\theta_F \approx 1$), then the number of oxygen atoms on the surface is negligible ($\theta_O \approx 0$) and the number of vacant sites is very small ($\theta_v \ll 1$), therefore equation (7) can be simplified to:

$$\omega = \frac{\Gamma}{\sigma} k_{O,A} \theta_v^{n_{O,A}} \tag{10}$$

Denote $b = n_{O,A} / n_{F,A}$ the ratio of the orders of adsorption of fuel and oxygen. It can be shown [9], that ratio b should always be greater or equal to one in catalytic ignition systems with initial fuel coverage.

If $b = 1$, then $n_{O,A} = n_{F,A}$, $n_{O,A} - n_{F,A} = 0$, $\theta_v^{n_{O,A} - n_{F,A}} = 1$ and the overall reaction rate is:

$$\omega = \frac{\Gamma}{\sigma} \frac{k_{F,D} k_{O,A}}{k_{F,A} - k_{O,A}} = \frac{\Gamma}{\sigma} \frac{k_{F,D}}{\dfrac{k_{F,A}}{k_{O,A}} - 1} \tag{11}$$

From equations (5) and (11):

$$\frac{\partial}{\partial T}\left(\frac{\Gamma k_{F,D}}{\sigma \dfrac{k_{F,A}}{k_{O,A}} - 1}\right) \Delta_r H = \frac{\lambda}{l_c} \tag{12}$$

Carrying out the differentiation, and substituting the above expressions for the rate coefficients, the following condition of ignition is obtained:

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$$\frac{\Gamma \Delta_r H \, L_c \, A_{F,D} \, E_{F,D} \exp(-E_{F,D} / RT)}{\lambda RT^2 \left(\sigma \dfrac{X_F}{X_O} \dfrac{S_{F,0}}{S_{O,0}} \sqrt{\dfrac{W_O}{W_F}} - 1 \right)} = 1 \tag{13}$$

The kind of quantity calculated on the left-hand-side of this equation is called [9] the ignition Damköhler number Δ_I. In equation (13), parameters $A_{F,D}$, $E_{F,D}$ and $S = S_{F,0}/S_{O,0}$ are physical constants of adsorption and desorption. Knowing these values and the other constants characteristic for the reaction and the experimental setup, ignition temperature T can be calculated knowing the composition of the gas by solving equation (13). On the other hand, this equation can be used for the determination of adsorption and desorption parameters from the experimental ignition temperature vs. gas composition data by nonlinear least-squares fitting.

If the ratio of the adsorption orders $b > 1$, then $n_{O,A} - n_{F,A} > 0$ and therefore, $\theta_v^{n_{O,A} - n_{F,A}} \approx 0$ if $\theta_v \ll 1$. This results in the following approximate expression for the overall reaction rate:

$$\omega = \frac{\Gamma k_{O,A}}{\sigma} \left(\frac{k_{F,D}}{k_{F,A}} \right)^b \tag{14}$$

Substituting equation (14) into equation (5) and differentiating all temperature dependent terms with respect to T results in the following equation:

$$\frac{\Delta_r H \, L_c \Gamma}{\lambda \sigma} \underbrace{\left(\frac{S_{0,0} A_{F,D}^b}{S_{F,0}^b} \right)}_{A^*} \left(\frac{\Gamma \sqrt{2\pi RT}}{p} \right)^{b-1} \frac{X_O / \sqrt{W_O}}{\left(X_F / \sqrt{W_F} \right)^b} \left(\frac{b-1}{2T} + b \frac{E_{F,D}}{T^2} \right) \exp\left(\frac{-bE_{F,D}}{RT} \right) = 1 \tag{15}$$

Using equation (15), ignition temperature T can be calculated from the composition of the gas knowing the physical constants and data of experimental setup. On the other hand, if ratio b of the adsorption reaction orders is known, $E_{F,D}$ and A^* can be obtained from a nonlinear least-squares fitting from experimental ignition temperature - gas composition data. If b is not known, its value can also be determined this way.

Initial oxygen coverage. If initially the surface is almost completely covered with oxygen ($\theta_O \approx 1$), then the ratio of the fuel on the surface is negligible ($\theta_F \approx 0$) and the number of vacant sites is very small ($\theta_v \ll 1$). This case can be treated analogously to the case of full fuel coverage. It can be shown [9], that the ratio of the adsorption orders $b = n_{O,A} / n_{F,A}$ should always be less or equal to one in catalytic ignition systems with initial oxygen coverage.

In the case of $b = 1$, the condition of ignition can be obtained using similar steps as shown in the case of fuel coverage:

$$\frac{\Gamma \Delta_r H \, L_c \, A_{O,D} \, E_{O,D} \exp(-E_{O,D} / RT)}{\lambda RT^2 \left(\dfrac{X_O}{X_F} \sqrt{\dfrac{W_F}{W_O}} \dfrac{S_{O,0}}{S_{F,0}} - \sigma \right)} = 1 \tag{16}$$

If $b < 1$, then the condition of ignition is the following:

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$$\frac{\Delta_r H \, l_c \Gamma}{\lambda} \underbrace{\left(\frac{S_{F,0} A_{O,D}^{1/b}}{S_{O,0}^{1/b}}\right)}_{A^*} \left(\frac{\Gamma\sqrt{2\pi RT}}{p}\right)^{1/b-1} \frac{X_F/\sqrt{W_F}}{\left(X_O/\sqrt{W_O}\right)^{1/b}} \left(\frac{1/b-1}{2T} + \frac{1}{b}\frac{E_{O,D}}{RT^2}\right) \exp\left(\frac{-E_{O,D}}{bRT}\right) = 1 \quad (17)$$

Equations (16) and (17) can be used the same way as described in the case of full fuel coverage. Note that in the case of oxygen coverage, obtained activation energy and preexponential factor values describe oxygen desorption.

Determination of Parameters by Fitting Experimental Data

We have found more than 50 publications dealing with heterogeneous ignition. Most experimental data of heterogeneous ignition are available for the ignition of H_2, CO, CH_4, but some papers were found that investigated the heterogeneous ignition of other fuels, including ethene and propene. These articles studied heterogeneous ignition on a polycrystalline platinum catalyst. Ignition temperature measurements showed that increasing the fuel/oxygen ratio, the ignition temperature increases in the case of CO, H_2, ethene, and propene, whereas the ignition temperature decreases in the case of CH_4.

In this section, published experimental ignition temperature measurements were reanalysed using the analytical expressions derived on the dependence of ignition temperature from experimental and physical parameters. In all cases, the experimental data were digitised from the original publications and the experimental conditions were extracted from the text of the article. The utility programs of the CHEMKIN-II package [17] were used for the calculation of parameters like thermal conductivity and viscosity of gas mixtures at a given temperature. Knowing the experimental conditions, equations (13), (15), (16), (17) relate ignition temperature to physical parameters, like ratio of sticking coefficients and Arrhenius parameters of desorption. The nonlinear implicit algebraic equations were solved numerically to obtain the ignition temperature. The experimental ignition temperature vs. gas composition data can be fitted using these equations to obtain the unknown physical parameters. The Levenberg-Marquardt (LM) algorithm encoded by P. Holpár and E. Keszei [18] was used for the nonlinear least-squares fits.

An important question is if the parameters to be determined are effective and/or independent of each other. Principal component analysis [19] of local sensitivity matrix is an efficient method to answer such type of questions. First, the parameters determined by the previous nonlinear least-squares fitting were utilized for computing T_i^c, the calculated ignition temperature at the conditions of experiment i. In the next step, parameters E_D, S and A_D were changed by 0.1% and sensitivity coefficients $(s_{i1}, s_{i2}, s_{i3}) = (\partial T_i^c/\partial E_D, \partial T_i^c/\partial S, \partial T_i^c/\partial A_D)$ were estimated via the calculation of finite differences. The sensitivity coefficients were then normalized by calculating $\left(E_D/T_i^c\right)\left(\partial T_i^c/\partial E_D\right)$, $\left(S/T_i^c\right)\left(\partial T_i^c/\partial S\right)$, and $\left(A_D/T_i^c\right)\left(\partial T_i^c/\partial A_D\right)$. The normalized sensitivity vectors form matrix $\tilde{\mathbf{S}}$, which have 3 columns and i rows. According to the method of the principal component analysis of local sensitivity matrices [19], eigenvectors of matrix $\tilde{\mathbf{S}}^T\tilde{\mathbf{S}}$ show if the parameters are independent of each other and the corresponding eigenvalues indicate the effectiveness of single parameters or parameter groups defined by the eigenvectors. For example, in case of three parameters, eigenvector (1.00, 0.00, 0.00) means that the first parameter is independent from the other two; eigenvector (0.00, −0.71, 0.71) related to a high eigenvalue means that the model output is determined by the ratio of the 2nd and 3rd parameters. The effectiveness of a parameter within a parameter group can be characterized by the square of the corresponding eigenvector

component. The principal component analysis calculations were performed using a modified version of KINAL [20].

Ignition of CO on polycrystalline Pt surface. Heterogeneous ignition of CO on platinum surfaces has been discussed in numerous papers but only few of them [1, 12, 21] contain original experimental data. When the fuel/oxygen ratio is increased, the ignition temperature in the $CO/O_2/Pt$ system increases, which indicates that the surface of the catalyst is initially covered with the fuel; therefore equations (13) and (15) are to be used in this case. Experimental CO ignition data of Cho and Law [1] and Rinnemo et al. [12] were fitted using equations (13) and (15). These articles contain data for the "wire in flow" geometry. The two datasets were fitted simultaneously.

The first step is to determine the ratio of adsorption orders, which was performed using equation (15), where the ratio of adsorption orders b was one of the fitting parameters. Principal component analysis indicated that b is an independent and effective parameter in this case. The determined value was $b=1.03\pm0.10$. Therefore, the adsorption reaction orders of CO and O_2 can be assumed to be equal. Next, assuming that $b=1$, a nonlinear least-squares fitting was performed using equation (13) to obtain values of $E_{CO,D}$, $S=S_{CO,0}/S_{O_2,0}$, and $A_{CO,D}$. Relatively high error limits suggested that these parameters could be interdependent, which was verified with a principal component analysis of the normalized sensitivity matrix. Results of the principal component analysis show that ratio A_D/S could be fitted independently and effectively. Therefore, equation (13) was transformed to the following form:

$$\frac{\Gamma \Delta_r H \, L_c \left(\frac{A_{T,D}}{S} \right) E_{F,D} \, \exp\left(- E_{F,D} / RT \right)}{\lambda RT^2 \left(\sigma \frac{X_F}{X_O} \sqrt{\frac{W_O}{W_F}} - \frac{1}{S} \right)} - 1 \tag{18}$$

Using this equation, the fitting parameters now are E_D, A_D/S and $1/S$. Results of the principal component analysis of equation (18) indicates that all new fitting parameters can be determined separately, though A_D/S is not a very effective parameter, therefore it will have higher standard deviation.

The results of parameter estimation are: $E_{CO,D}= 107.2\pm12.7$ kJ/mol, $A_{CO,D}/S= (9.74\pm19.57)\times10^{11}$, and $1/S=0.0243\pm0.0050$. The indicated errors are 95% confidence limits. These determined parameters were transformed to the mean values of parameters $E_{CO,D}$, S, and $A_{CO,D}$ and the corresponding 95% confidence limits, taking into account the rules of error propagation. The determined activation energy of desorption of CO from polycrystalline Pt surface was $E_{CO,D} = 107.2\pm12.7$ kJ/mol. The ratio of the zero coverage sticking coefficients is $S_{CO,0}/S_{O_2,0}= 41.2\pm8.5$, and the preexponential factor of the CO desorption is $A_{CO,D}=4.0\times10^{13}\pm8.1\times10^{13}$ s^{-1}.

Ignition of H_2 on polycrystalline Pt surface. Catalytic ignition of H_2 on Pt surfaces has been discussed in several papers, many of which reanalysed the same original measurements. Original experimental ignition temperature data were published in references [1, 11, 22, 23, 24, 25]. Similarly to the $CO/O_2/Pt$ system, the ignition temperature in the $H_2/O_2/Pt$ system increases with the increasing fuel/oxygen ratio. This indicates that the surface of the catalyst is covered with the fuel, therefore equations (13) and (15) are valid. Ignition temperature vs. gas composition data obtained by Fassihi et al. [22] and Deutschmann et al. [25] were reanalysed using equations (13) and (15). Fassihi et al. used "wire in flow" setup, whereas Deutschmann et al. used "stagnation point flow" setup. Although the experimental conditions

were very different, both datasets could be fitted simultaneously and the experimental data could be reproduced with the same physical parameters.

Determination of the ratio of adsorption orders was carried out using equation (15), and $b=1.08\pm0.15$ was found. Again, principal component analysis indicated that b is an independent and effective parameter in this case. Therefore, it can be assumed that the adsorption reaction orders of H_2 and O_2 are equal, that is, $b=1$. This means that either equation (13) or equation (18) can be used, depending on the result of the principal component analysis. Principal component analysis informed us that the fitting parameters A_D, E_D, and S in equation (13) are interdependent; consequently the transformed equation (18) was used for the nonlinear least-squares fitting. The results of the parameter estimation are the following: $E_{H_2,D}$ 43.3 ± 5.2 kJ/mol, $A_{H_2,D}/S=(2.57\pm3.9)\times10^{11}$ and $1/S=0.0272+0.0071$. The determined parameters were transformed to the mean values and 95% confidence limits of parameters $E_{H_2,D}$, S and $A_{H_2,D}$, taking into account the rules of error propagation. The determined value of the activation energy of the desorption of H_2 from Pt surface is $E_{H_2,D}$ 43.3 ± 5.2 kJ/mol. The ratio of the zero coverage sticking coefficients is $S_{H_2,0}/S_{O_2,0}=36.7\pm9.6$, and the preexponential factor of the H_2 desorption is $A_{H_2,D}$ $9.43\times10^{12}\pm14.5\times10^{12}$ s^{-1}.

Ignition of alkenes on polycrystalline Pt surface. Olefin molecules are easily adsorbed by rupturing the weak carbon-carbon π-bond and forming two separate carbon–metal σ-bonds. The ignition temperature in this system increases with the increasing fuel/oxygen ratio, indicating that the surface is covered with the fuel. This means that equations (13) and (15) are applicable.

Two papers [1, 6] were found that investigated the dependence of the heterogeneous ignition temperature of alkenes on the composition of the gas. Veser and Schmidt [6] published ignition temperature data of ethene and propene obtained in stagnation point flow geometry, while Cho and Law [1] studied ethene and propene ignition in 'wire in flow' geometry.

Ignition of ethene. Experimental data of Cho and Law [1] were fitted using equations (13) and (15). Determination of the ratio of adsorption orders was performed using equation (15), and $b = 1.03\pm0.17$ was obtained. Principal component analysis showed that b could be determined independently and effectively in this case. Thus, it can be assumed that the adsorption reaction orders of ethene and oxygen are equal. Assuming that $b = 1$, a nonlinear least-squares fitting and a subsequent principal component analysis was performed, using equation (13). Principal component analysis indicated that the fitting parameters A_D, E_D, and S can be determined independently in this case, although the ignition temperature is relatively insensitive to the value of A_D. The results of the parameter estimation are: $E_{C_2H_4,D} = 135.6\pm20.95$ kJ/mol, $S_{C_2H_4,0}/S_{O_2,0} = 15.6\pm1.9$, $A_{C_2H_4,D} = (5.522\pm16.29)\times10^{11}$ s^{-1}. The indicated errors are 95% confidence limits. The measured data and the fitted curves are shown in Figure 1.
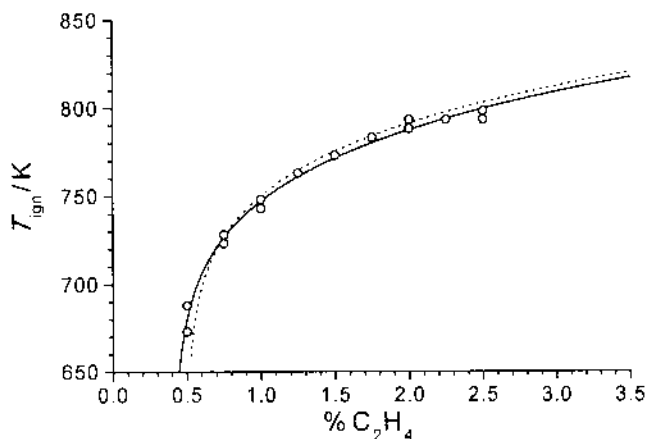
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Figure 1. Surface ignition temperature for ethene ignition. Circles show the experimental data of Cho and Law [1]; the solid and the dashed lines denote the fitted curves using equations (13) and (15), respectively.

Ignition of propene. Heterogeneous ignition temperature data of Cho and Law [1] were used for the determination of adsorption and desorption parameters of propene on polycrystalline platinum. Using equation (15), the ratio of adsorption orders $b = 1.05\pm0.33$ was determined. Assuming that $b = 1$ and using equation (13), the parameter estimation gave the following results: $E_{C_3H_6,D} = 160.8\pm52.91$ kJ/mol, $S_{C_3H_6,0}/S_{O_2,0} = 11.9\pm1.7$, $A_{C_3H_6,D} = (1.20\pm9.32)\times10^{13}$ s^{-1}. The indicated errors are 95% confidence limits. Principal component analysis of equation (13) proved that the determined parameters could be determined independently. The standard deviations are higher in this case because only few measured ignition temperature data were available and their scatter was significant.

Ignition of CH$_4$ on polycrystalline Pt surface. Unlike in the case of the heterogeneous ignition of CO, H$_2$, and alkenes, which were discussed above, increasing the fuel/oxygen ratio in the CH$_4$/O$_2$/Pt system results in lower ignition temperature. This indicates that the surface of the catalyst is initially covered with oxygen atoms, and equations (16) and (17) are to be used. Note that these equations contain the activation energy and the preexponential factor of the desorption of oxygen and not of the methane. Experimental data obtained by Veser and Schmidt [6] were reanalysed using equations (16) and (17). Determination of the ratio of adsorption orders was carried out using equation (17), and $b=0.95\pm0.25$ was found, therefore the adsorption reaction orders were considered to be equal. Equation (16) was used to determine values $E_{O_2,D}$, $A_{O_2,D}$, and $S = S_{O_2,0} / S_{CH_4,0}$, and the following results were obtained: $E_{O_2,D}=190\pm34$ kJ/mol, $A_{O_2,D}=(7.5\pm35)\times10^{13}$ s^{-1}, and $S=5.9\pm0.3$. The independency and effectiveness of these parameters were checked by a subsequent principal component analysis, which showed that the parameters could be determined independently, although the preexponential factor $A_{O_2,D}$ is not a very effective parameter, therefore its value has a large error limit.

Conclusions

A new method has been developed for the evaluation of heterogeneous ignition temperature measurements using an analytical model, which is based on the analysis of the heat balance and the Frank–Kamenetskii condition. Equations were deduced to relate the ignition temperature to the gas composition, the experimental parameters, and the physical parameters of the adsorption/desorption processes. These equations can be used to predict the ignition temperature as a function of the gas composition, if the physical parameters of the adsorption and desorption and the parameters of the experimental setup are known. On the other hand, these equations can be applied to evaluate heterogeneous ignition temperature measurements and to obtain unknown physical parameters by means of nonlinear least-squares fitting.

This method was used to re-evaluate experimental ignition temperature data for the following systems: $CO/O_2/Pt$, $H_2/O_2/Pt$, $C_2H_4/O_2/Pt$, $C_3H_6/O_2/Pt$, and $CH_4/O_2/Pt$. Activation energy values were determined for the desorption of CO, H_2, C_2H_4, C_3H_6, and O_2 from polycrystalline platinum surface. In addition, ratios of the zero coverage sticking coefficients, and ratio of the adsorption reaction orders were also determined.

Design and optimisation of heterogeneous and catalytically stabilized thermal (CST) combustors and catalytic three-way converters require the proper quantitative description of heterogeneous ignition and combustion. However, most of the data used in numerical models are either crude estimations or based on physical measurements at very different conditions, like on a single crystal at low temperature. The method described here allows the determination of basic parameters of adsorption and desorption, corresponding to a practical catalyst at the temperature of ignition, that are essential for the computer simulation of heterogeneous combustion systems. The parameters determined are directly applicable in numerical modelling.

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