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Determination of the adsorption and desorption parameters for ethene and propene from measurements of the heterogeneous ignition temperature

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Abstract

If a cold catalyst is exposed to a mixture of fuel + oxygen, the surface coverage of the catalyst can be dominated by either the fuel or the oxygen, depending on the actual catalyst and the composition of the gaseous mixture. If the temperature is increased, heterogeneous ignition occurs; the ignition temperature is influenced by the adsorption and desorption properties of both the fuel and the oxygen. Based on the equations for the heat balance, expressions have been derived for calculating the ignition temperature from the parameters of the experimental setup and the adsorption and desorption parameters of the fuel and the oxygen. These expressions can also be used to evaluate measured ignition temperatures to determine unknown adsorption and desorption parameters, such as the pre-exponential factor A_D and activation energy E_D for the desorption of the dominant surface species, the ratio of the sticking coefficients, and the ratio of the adsorption orders of the fuel and oxygen. This latter approach was used to evaluate measurements made by Cho and Law for the catalytic ignition of ethene and propene on polycrystalline platinum. The following parameters were determined by means of nonlinear least-squares fitting: $E_D(\text{C}_2\text{H}_4/\text{Pt}) = 136 \pm 21$ kJ/mol, $E_D(\text{C}_3\text{H}_6/\text{Pt}) = 161 \pm 53$ kJ/mol, $S_{\text{C}_2\text{H}_4,0}/S_{\text{O}_2,0} = 15.6 \pm 1.9$, $S_{\text{C}_3\text{H}_6,0}/S_{\text{O}_2,0} = 11.9 \pm 1.7$. Using a previously determined value for the sticking coefficient of O_2 , the values $S_{\text{C}_2\text{H}_4,0} = 0.38 \pm 0.08$ and $S_{\text{C}_3\text{H}_6,0} = 0.29 \pm 0.06$ were obtained. These error limits refer to a confidence level of 0.95. Experimental ignition temperatures could be reproduced assuming second order adsorption of ethene and propene on a surface of Pt.

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Keywords: Heterogeneous ignition; Adsorption kinetics; Activation energy of desorption; Sticking coefficient; Polycrystalline platinum; Alkenes; Oxygen

1. Introduction

If a bare catalyst is exposed to a mixture of a gaseous fuel and oxygen below its ignition temper-

ature, the surface becomes covered by both fuel and oxygen. Depending on the conditions, either the fuel or the oxygen has a higher coverage. If the fuel initially has a higher coverage, all the oxygen atoms bound to the surface are consumed soon by surface reactions. The vacant sites will also be covered mainly by species of the fuel, and again adsorbed oxygen atoms will be fully consumed. There-

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Nomenclature

$A_{i,D}$	Pre-exponential factor of desorption of species i [s^{-1}]	$S_{i,0}$	Zero coverage sticking coefficient of species i [—]
$A'_{i,D} = A_{i,D}\theta_i^{n_{i,D}}$	Apparent pre-exponential factor of desorption of species i [s^{-1}]	T	Temperature of the catalyst [K]
$b = n_{O,A}/n_{F,A}$	Ratio of the reaction orders of adsorption of fuel and oxygen [—]	T_∞	Temperature of the inlet gas flow far from the catalyst [K]
d	Diameter of the catalytic wire [m]	u	Gas flow velocity [$m\ s^{-1}$]
$E_{i,D}$	Activation energy of desorption of species i [$J\ mol^{-1}$]	W_i	Molar mass of species i [$kg\ mol^{-1}$]
f_r	Roughness factor of the catalyst surface [—]	X_i	Mole fraction of species i in gas phase [—]
k	Number of surface sites occupied by the oxidation products [—]	<i>Greek</i>	
$k_{i,A}$	Rate coefficient of adsorption of species i [s^{-1}]	Γ	Number of active catalytic sites per unit geometric surface area [$mol\ m^{-2}$]
$k_{i,D}$	Rate coefficient of desorption of species i [s^{-1}]	Γ_0	Number of active catalytic sites per unit real catalytic surface area [$mol\ m^{-2}$]
L_c	Characteristic thermal length (equivalent width of the boundary layer above the catalyst) [m]	$\Delta_r H$	Molar enthalpy of the overall reaction [$J\ mol^{-1}$]
L'_c	Reduced characteristic thermal length [m]	θ_i	Surface coverage of species i [—]
m	Number of surface sites occupied by each molecule of the fuel [—]	θ_v	Surface coverage of vacant sites [—]
$n_{i,A}$	Reaction order of adsorption of species i [—]	κ	Factor describing the rate of heat loss through the solid structure (corresponding to unit geometric surface area) [$W\ m^{-2}\ K^{-1}$]
$n_{i,D}$	Reaction order of desorption of species i [—]	λ	Heat conductivity of the gas [$W\ m^{-1}\ K^{-1}$]
p	Pressure in the gas phase [Pa]	ν	Kinematic viscosity of the gas [$m^2\ s^{-1}$]
p_i	Partial pressure of species i in gas phase [Pa]	σ	Number of oxygen molecules required for the oxidation of one molecule of the fuel [—]
Q_e	Rate of heat production due to electric heating (corresponding to unit geometric surface area) [$W\ m^{-2}$]	ω	Rate of the overall reaction (corresponding to unit area) [$mol\ m^{-2}\ s^{-1}$]
R	Universal gas constant [$J\ mol^{-1}\ K^{-1}$]	<i>Subscripts</i>	
Re	Reynolds number [—]	A	adsorption
$S = S_{F,0}/S_{O,0}$	Ratio of zero coverage sticking coefficients of fuel and oxygen [—]	D	desorption
		i	designation of the surface species
		F	fuel
		O	oxygen

fore, in a few such steps, the surface becomes almost fully covered by fuel species. In this case, if the concentration of fuel in the gas phase is increased, the mixture becomes less reactive and ignition happens at a higher temperature. This means that increasing the ratio of fuel/oxygen in the gas mixture raises the ignition temperature. The systems: $H_2/O_2/Pt$ [1], $CO/O_2/Pt$ [1], ethene/ O_2/Pt [1], propene/ O_2/Pt [1–3], and $NH_3/O_2/Pt$ [4] show such behavior. In the opposite case, the surface is initially almost fully covered with oxygen atoms, and increasing the fuel/oxygen ratio lowers the ignition temperature. Such systems are $CH_4/O_2/Pt$ [4–6], $C_2H_6/O_2/$

Pt [6,7], propane/ O_2/Pt [1,4,5,8], and butane/ O_2/Pt [1,8].

Recently, a new method [9] for evaluating measurements of heterogeneous ignition temperatures has used an analytical model based on the heat balance and the Frank–Kamenetskii condition. It was assumed there that the overall reaction rate is limited by the rate of adsorption of the less efficiently adsorbed reactant, which in turn depends on the desorption of the more efficiently adsorbed reactant. Equations were deduced to relate the ignition temperature to the gas composition, the experimental parameters, and the physical parameters of adsorption and desorption. These equa-

tions can be used to predict the ignition temperature as a function of the composition of the gas, if the physical parameters for the adsorption and desorption and also some parameters of the experimental setup are known. On the other hand, the same equations can be applied to interpret measured heterogeneous ignition temperatures and so obtain unknown physical parameters via nonlinear least-squares fitting. This method has been used [9] to determine the activation energy for the desorption of CO, H₂, and O₂ from a polycrystalline platinum surface. In addition, the ratios of the sticking coefficients (at zero coverage): $S_{\text{CO},0}/S_{\text{O}_2,0}$, $S_{\text{H}_2,0}/S_{\text{O}_2,0}$, and $S_{\text{O}_2,0}/S_{\text{CH}_4,0}$, and the ratios of adsorption orders were also determined. In this paper, the same procedure is employed to determine the parameters for the adsorption and desorption of ethene and propene.

The parameters determined here not only have scientific significance, but are also important from a practical point of view. The partial oxidation of ethene and propene on a catalytic surface is important in the petrochemical industry, e.g., in the catalytic conversion of hydrocarbons [10–12]. Another important area is the optimization of three-way catalytic converters used after internal combustion engines. Such converters simultaneously reduce NO and oxidize CO and the unburnt hydrocarbons, mainly consisting of ethene and propene. Chatterjee et al. [13] have modeled a single channel of a monolithic converter, assuming a two-dimensional flow field, coupled with a detailed model for surface reactions. In this model, C₃H₆ represented the unburnt hydrocarbons. The catalyst was assumed to be Pt/Rh and the model included a detailed mechanism for the oxidation of propene on the Pt sites only. In this mechanism, values of A_{D} , E_{D} , and $S_{\text{C}_3\text{H}_6,0}$ from Tsai et al. [14] were used. The model used by Chatterjee et al. [13] reproduced well all the measured conversions, except for the conversion of C₃H₆ in rich mixtures. A further improved version of their model, taking into account the flow and the heat distribution in the whole monolithic converter and using a more accurate mechanism for the oxidation of propene, could be an effective tool for the design and optimization of automotive catalysts.

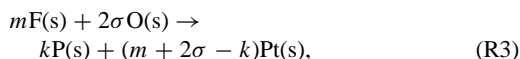
2. Analytical expressions for calculating an ignition temperature

The reaction of a gaseous fuel with oxygen on a catalytic surface can be described by



The details of the elementary steps can be very complicated, but must contain the equilibria for the competitive adsorption and desorption of both the

fuel and oxygen, as well as the reaction of adsorbed species on the surface and the desorption of reaction products [15]:



The symbols F, O₂, and P denote molecules of the fuel, oxygen, and the product, respectively, in the gas phase; F(s), O(s), and P(s) denote adsorbed species of the fuel, an oxygen atom, and the product, respectively; Pt(s) denotes a vacant site. Adsorption of a molecule of fuel requires m vacant sites. Note that step (R3) can be either an elementary reaction on the surface, or an overall reaction incorporating all surface reactions.

In catalytic ignition experiments, a frequently used experimental setup is an electrically heated catalytic wire or plate, placed vertically in a cross-flow of gas [1,16,17]. In most experiments, platinum wires or plates have been used, although some measurements have been carried out also with palladium [7, 18], iridium [7,18], rhodium [7,18], and nickel [7] catalysts. In such experiments, the temperature of the catalyst was increased to just below the ignition temperature. Having reached a steady state, a small extra heating ignited the system and the temperature was recorded at increasing times, until a new steady state was achieved. Due to the exothermicity of the chemical reaction and also the external heating, the temperature T of the surface of the catalyst was always higher than the temperature T_∞ of the inlet gas. The temperature, T , was determined by the heat balance; i.e., the heat produced by the electric heating and by the chemical reactions is equal to the heat loss. Due to the relatively low temperature, conductive and radiative heat transport could be neglected and heat was lost mainly due to cooling of the catalyst by the flowing gas. According to the theory of heat transfer [19], the rate of convective heat loss depends linearly on $(T - T_\infty)$ and is proportional to the ratio of the heat conductivity, λ , of the gas and the characteristic thermal length, L_c , i.e.,

$$\omega \Delta_r H + Q_e = \frac{\lambda}{L_c} (T - T_\infty). \quad (2)$$

Here $\Delta_r H$ is the enthalpy of the overall reaction, ω is the rate of the overall reaction, and Q_e is the rate of heat production due to electric heating. If the heat loss through the solid structure cannot be neglected, it can be taken into consideration with a further linear

term, giving

$$\begin{aligned}\omega\Delta_r H + Q_e &= \frac{\lambda}{L'_c}(T - T_\infty) + \kappa(T - T_\infty) \\ &= \frac{\lambda}{L'_c}(T - T_\infty).\end{aligned}\quad (3)$$

Here, κ is a constant for the rate of heat loss through the solid structure. The value of κ depends on many factors and is difficult to determine; however, for a given experimental setup this value is constant. L'_c is the reduced characteristic thermal length for the actual experimental setup:

$$L'_c = \frac{L_c}{1 + \kappa L_c/\lambda}.\quad (4)$$

If κ is zero or negligibly small, then $L'_c = L_c$.

The characteristic thermal length L_c can be calculated [19] for a wire of diameter d , placed perpendicular to a flow of velocity u , as

$$L_c = \frac{d}{0.891 \times 10^2 \text{Re}^{0.33}},\quad (5)$$

where Re is the Reynolds number ($\text{Re} = ud/\nu$) and ν is the kinematic viscosity of the gas at temperature T_∞ .

Before ignition, the surface temperature is determined by a balance of the rates of electric heating, the heat produced by surface reactions, and the heat loss; the rate of electric heating is more significant than that of the chemical reactions. Any increase in surface temperature requires additional electric heating. At the ignition temperature, an infinitesimal increase in the external heating results in a large change in surface temperature. At the moment of ignition, the temperature increases spontaneously due to the chemical reactions, without additional heating. According to the Frank-Kamenetskii condition [20], differentiating Eq. (3) with respect to temperature results in the following condition for ignition:

$$\frac{\partial\omega}{\partial T}\Delta_r H = \frac{\lambda}{L'_c}.\quad (6)$$

In this equation, λ and L'_c can be calculated from the conditions of the experiment and $\Delta_r H$ is well known. The rate of the overall reaction, ω , can be obtained from the differential equations for the surface coverage of the species. However, due to the stoichiometry of the reaction steps, the overall reaction rate and the time derivatives of the surface coverage of the species are not independent. The following equations relate overall rate, ω , to the rate coefficients for 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 orders of reaction of adsorption and desorption of the fuel and oxygen ($n_{F,A}$, $n_{F,D}$, $n_{O,A}$, $n_{O,D}$):

$$\frac{\omega}{\Gamma} = k_{F,A}\theta_v^{n_{F,A}} - k_{F,D}\theta_F^{n_{F,D}},\quad (7)$$

$$\frac{\omega}{\Gamma} = \frac{1}{\sigma}(k_{O,A}\theta_v^{n_{O,A}} - k_{O,D}\theta_O^{n_{O,D}}).\quad (8)$$

In these equations, Γ is the number of active catalytic sites per unit geometric surface area. For a smooth Pt catalyst, the geometric surface area equals the active catalytic surface area. Therefore, $\Gamma = \Gamma_0 = 2.71 \times 10^{-5} \text{ mol m}^{-2}$ [21], where Γ_0 is the density of active sites on a Pt surface. For rough surfaces, the active catalytic area is larger than the geometric surface area, and the surface roughness factor, f_r , has to be taken into consideration, with $\Gamma = f_r\Gamma_0$.

The rate coefficient, $k_{i,A}$, for the adsorption of species i at zero surface coverage is equal to the number of species hitting the surface in unit time multiplied by the zero-coverage sticking coefficient $S_{i,0}$ [22],

$$k_{i,A} = \frac{S_{i,0}p_i}{\Gamma(2\pi W_i RT)^{1/2}} = \frac{S_{i,0}pX_i}{\Gamma(2\pi W_i RT)^{1/2}},\quad (9)$$

where W_i , p_i , and X_i are the molar mass, the partial pressure, and the mole fraction of species i in the gas phase, respectively.

The rate coefficient for desorption can be described by the Arrhenius expression:

$$k_{i,D} = A_{i,D}\exp(-E_{i,D}/RT).\quad (10)$$

If initially the surface is almost completely covered with fuel ($\theta_F \approx 1$), the number of oxygen atoms on the surface is negligible ($\theta_O \approx 0$), and the number of vacant sites is very small ($\theta_v \ll 1$), then Eqs. (7) and (8) can be simplified to

$$\omega = \Gamma(k_{F,A}\theta_v^{n_{F,A}} - k_{F,D}),\quad (11)$$

$$\omega = \frac{\Gamma}{\sigma}k_{O,A}\theta_v^{n_{O,A}}.\quad (12)$$

The constraints $\theta_F \approx 1$, $\theta_O \approx 0$, and $\theta_v \ll 1$ hold, if the desorption of the fuel is the rate-limiting step in the reaction mechanism. If the fuel decomposes on the surface before oxidation, but the rate-limiting step is still the desorption of the unreacted fuel, the surface is covered with the fuel and its decomposition products. If only molecules of the unreacted fuel desorb, the rate of desorption is lower due to the lower surface coverage of the unreacted fuel. In this case, an apparent pre-exponential factor $A'_{F,D} = A_{F,D}\theta_F^{n_{F,D}}$ should be used in Eq. (10) instead of A , where θ_F is the surface coverage of the undecomposed fuel species. This approach is valid if the steady state ratio of decomposed and undecomposed species on the surface does not depend on the temperature below the ignition temperature. If this ratio is temperature-dependent, the activation energy $E_{F,D}$ in Eq. (10) should account also for this temperature dependence.

If one of the elementary steps of oxidation is rate-limiting, the surface is probably covered with both fuel and oxygen, and the ratio of the adsorbed fuel and oxygen would depend on the gas composition. In this last case, Eqs. (7) and (8) cannot be simplified, so a more detailed model has to be used to describe the surface reactions.

Defining $b = n_{O,A}/n_{F,A}$, the ratio of the orders of adsorption of fuel and oxygen, it can be shown [9] that b should always be greater than or equal to one in catalytic ignition systems with initial fuel coverage. If $b = 1$, then $n_{O,A} = n_{F,A}$, $n_{O,A} - n_{F,A} = 0$, and $\theta_v^{n_{O,A} - n_{F,A}} = 1$. Expressing θ_v from Eq. (12) and substituting it into Eq. (11) gives the overall reaction rate as

$$\omega = \frac{\Gamma k_{F,D} k_{O,A}}{\sigma k_{F,A} - k_{O,A}} = \frac{\Gamma k_{F,D}}{\sigma k_{F,A}/k_{O,A} - 1}. \quad (13)$$

From Eqs. (6) and (13),

$$\frac{\partial}{\partial T} \left(\frac{\Gamma k_{F,D}}{\sigma k_{F,A}/k_{O,A} - 1} \right) \Delta_r H = \frac{\lambda}{L'_c}. \quad (14)$$

Differentiating, and substituting expressions (9) and (10) for the rate coefficients, the following condition for ignition is obtained:

$$\frac{A_{F,D}}{L'_c} \frac{\Gamma \Delta_r H E_{F,D} \exp(-E_{F,D}/RT)}{RT^2 \left(\sigma \frac{X_F}{X_O} \left(\frac{W_O}{W_F} \right)^{1/2} \frac{S_{F,0}}{S_{O,0}} - 1 \right)} = 1. \quad (15)$$

The quantity calculated on the left-hand side of Eq. (15) is called [9] the ignition Damköhler number Δ_I . In Eq. (15), the parameters $A_{F,D}$, $E_{F,D}$, and $S = S_{F,0}/S_{O,0}$ are physical constants for adsorption and desorption. Therefore, in the case of $b = 1$, if these values and the other constants characteristic of the reaction and the experimental setup are known, the ignition temperature T can be calculated knowing the composition of the gas by solving Eq. (15). On the other hand, Eq. (15) can be used to determine the parameters for adsorption and desorption from a plot of the measured ignition temperature against the composition of the gas by nonlinear least-squares fitting.

If the ratio of the adsorption orders $b > 1$, $n_{O,A} - n_{F,A} > 0$ 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:

$$\omega = \frac{\Gamma k_{O,A}}{\sigma} \left(\frac{k_{F,D}}{k_{F,A}} \right)^b. \quad (16)$$

Substituting Eq. (16) into Eq. (6) and differentiating every temperature-dependent term with respect to T yields

$$\begin{aligned} & \frac{\Delta_r H \Gamma L'_c}{\sigma \lambda} \left(\frac{S_{O,0} A_{F,D}^b}{S_{F,0}^b} \right) \left(\frac{\Gamma (2\pi RT)^{1/2}}{p} \right)^{b-1} \\ & \times \frac{X_O/W_O^{1/2}}{(X_F/W_F^{1/2})^b} \left(\frac{b-1}{2T} + b \frac{E_{F,D}}{RT^2} \right) \\ & \times \exp \left(\frac{-b E_{F,D}}{RT} \right) = 1. \end{aligned} \quad (17)$$

Using Eq. (17), the ignition temperature T can be calculated from the composition of the gas, if the physical constants and information describing the experimental setup are known. On the other hand, if the ratio b of the adsorption reaction orders is known, then $E_{F,D}$ and $S_{O,0} A_{F,D}^b / S_{F,0}^b$ can be obtained from a nonlinear least-squares fit to the experimental ignition temperature, when plotted against the composition of the gas. If b is not known, its value can also be determined in this way.

The value of L'_c in Eqs. (15) and (17) can only be calculated, if the rate κ of heat loss through the solid structure attached to the catalyst is known. The determination of κ is not straightforward; in most cases, only a rough estimation can be made, so κ is generally unknown. However, Eqs. (15) and (17) can still be used to determine the adsorption and desorption parameters from the experimental ignition temperatures. If the heat loss through the solid structure is negligible, then, according to Eq. (4), L_c can be used instead of L'_c . L_c can be calculated using Eq. (5), and the adsorption and desorption parameters can be determined via a nonlinear parameter estimation. If κ is a significant parameter, L'_c differs from L_c . If the L_c calculated from Eq. (5) is used as L'_c , the values determined for the parameter $A_{F,D}$ (in the case of Eq. (15)) or $S_{O,0} A_{F,D}^b / S_{F,0}^b$ (in the case of Eq. (17)) will be biased. However, due to the structures of Eqs. (15) and (17), the determinations of $E_{F,D}$, $S = S_{F,0}/S_{O,0}$ and b are not affected, and the fitting provides unbiased values for these parameters, even if κ is significant. In our calculations, $A_{F,D}$ was never considered as a physical result due to its large confidence interval.

The roughness factor was assumed to be $f_r = 1.00$, which seems feasible for a platinum wire catalyst. Deviations in the roughness factor may cause an error in the determination of the pre-exponential factor, since the error of the roughness factor f_r propagates through an error in Γ , causing the determined pre-exponential factor to be biased; however, determination of the other parameters is not affected.

If the fuel decomposes on the surface before oxidation, the pre-exponential factor obtained via the nonlinear fitting to Eq. (15) is an apparent pre-exponential factor, $A'_{F,D} = A_{F,D} \theta_F^{n_{F,D}}$. If the steady state ratio of decomposed and undecomposed species on the surface does not depend on the temperature below the ignition temperature, the determinations

of $E_{F,D}$ and $S = S_{F,0}/S_{O,0}$ are not affected and the fitting will provide the correct values for these parameters. If the above ratio is temperature-dependent, this dependence may influence the determination of the activation energy; however, the value determined for $S = S_{F,0}/S_{O,0}$ is still valid.

3. Determination of the parameters by fitting experimental data

Most measurements of heterogeneous ignition are available for H_2 , CO , and CH_4 . Only two papers [1,5] were found on how the heterogeneous ignition temperature of alkenes depends on the composition of the gas. The data of Veser and Schmidt [5] on ethene and propene could not be used, because their description of the experimental setup lacked some required details. Catalytic ignition of ethene and propene on Pt surfaces has been studied by Cho and Law [1] using a Pt wire in flowing gas. CHEMKIN-II package [23] was used to calculate parameters like the thermal conductivity and the viscosity of gas mixtures at a given temperature. As the heat loss through the solid structure attached to the catalyst was not measured by Cho and Law [1], $\kappa = 0$ was assumed. This assumption may produce invalid values for the pre-exponential factor, if the heat loss through the solid structure is not negligible, but the other parameters are not affected.

Knowing the experimental conditions, depending on the value of b , Eqs. (15) or (17) can be used to relate ignition temperature to physical parameters, such as the ratio of sticking coefficients and the Arrhenius parameters for desorption. The nonlinear implicit algebraic equations were solved numerically to obtain the ignition temperature. The measured ignition temperatures at different gas compositions can be fitted using these equations to obtain the unknown physical parameters. The Levenberg–Marquardt (LM) algorithm, encoded by Holpár and Keszei [24], was used for the nonlinear least-squares fits.

An important question is whether the parameters to be determined are effective ones and/or independent of each other. Principal component analysis [25] of the local sensitivity matrices is an efficient way of answering such 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, the 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 by calculating finite differences. The sensitivity coefficients were then normalized by calculating $((E_D/T_i^c)(\partial T_i^c / \partial E_D), (S/T_i^c)(\partial T_i^c / \partial S), (A_D/T_i^c)(\partial T_i^c / \partial A_D))$. The normalized sensitivity

vectors form a matrix \tilde{S} , which has three columns and i rows. According to the method of principal component analysis of local sensitivity matrices [25], eigenvectors of the matrix $\tilde{S}^T \tilde{S}$ 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 the case of three parameters, the eigenvector (1.00, 0.00, 0.00) means that the first parameter is independent of the other two; the eigenvector (0.00, -0.71, 0.71), when related to a high eigenvalue, means that the output of the model is determined by the ratio of the second and third parameters. The effectiveness of a parameter within a group of parameters can be characterized by the square of the corresponding component of the eigenvector. The principal component analysis was performed using a modified version of KINAL [26].

4. Results for the ignition of ethene on a Pt surface

The overall reaction for the combustion of C_2H_4 is $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$; therefore, $\sigma = 3$. Using Eq. (17), the ratio b of the adsorption orders was one of the fitting parameters. Principal component analysis indicated that b is an independent and effective parameter in this case. The value determined was $b = 1.0 \pm 0.2$ and the corresponding fitted curve is given by the dashed line in Fig. 1. Also, assuming several possible integral adsorption orders, fitting was attempted based on Eq. (17) with the corresponding fixed values of b . A systematic deviation was found between the experimental data and the fitted curve for all cases, except for $b = 1$. Therefore, the adsorption reaction orders of C_2H_4 and O_2 can be assumed to be equal. Assuming that $b = 1$ and using Eq. (15), values of E_D , $S = S_{C_2H_4,0}/S_{O_2,0}$, and $A_{C_2H_4,D}$ were fitted. Principal component analysis at the parameter set of the best fit gave the following result: first parameter group: eigenvector (E : -0.995, S : -0.085, A : 0.000), eigenvalue 23.44; second parameter group: eigenvector (E : 0.083, S : -0.996, A : 0.000), eigenvalue 4.55×10^{-2} ; third parameter group: eigenvector (E : 0.052, S : 0.000, A : 0.998), eigenvalue 2.62×10^{-5} . This means that every parameter can be determined independently; the calculated ignition temperature is very sensitive to E_D , less sensitive to S , and not sensitive to the value of A_D . The results of parameter estimation are $E_D(C_2H_4/Pt) = 136 \pm 21$ kJ/mol, $S_{C_2H_4,0}/S_{O_2,0} = 15.6 \pm 1.9$, $A_D(C_2H_4/Pt) = (5.5 \pm 16.3) \times 10^{11}$ s $^{-1}$. The indicated errors are 95% confidence limits. The fitted curve is shown by the solid line in Fig. 1.

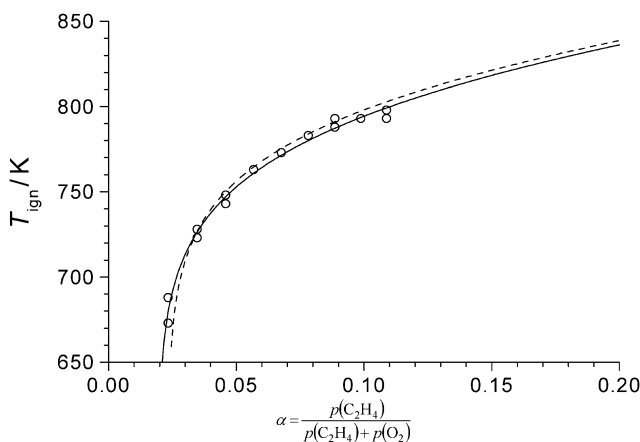


Fig. 1. Measured (circles) and calculated (lines) surface ignition temperature for the ignition of ethene. The dashed line shows the result when the value of b was determined using Eq. (17). The final parameters were obtained assuming $b = 1$ and using Eq. (15) (solid line).

This method can only determine the ratio b . Adsorption of O_2 on a polycrystalline Pt surface is usually assumed to be second order [16,27–31]. Therefore the ratio $b = 1$ means that the adsorption of ethene on a polycrystalline Pt surface is also of second order. The zero coverage sticking coefficient of O_2 on polycrystalline Pt has been determined [9] to be $S_{O_2,0} = 0.024 \pm 0.004$, using $S_{CO,0} = 1.00$, which is a measured [32] value for CO on polycrystalline Pt. Using this value of $S_{O_2,0}$ and the ratio $S_{C_2H_4,0}/S_{O_2,0}$ determined in this work, the zero coverage sticking coefficient of C_2H_4 on polycrystalline Pt is $S_{C_2H_4,0} = 0.38 \pm 0.08$, where the 95% confidence limit was calculated by taking into account the propagation of errors.

5. Results for the ignition of propene on a Pt surface

The overall reaction for the oxidation of propene is $C_3H_6 + 4.5O_2 \rightarrow 3CO_2 + 3H_2O$; therefore, $\sigma = 4.5$. The value of b was found to be $b = 1.1 \pm 0.3$ by fitting Eq. (17). Principal component analysis indicated that b is an independent and effective parameter in this case. The corresponding fitted curve is given by dashed line in Fig. 2. Just as the case of C_2H_4 , assuming several possible integral adsorption orders, a systematic deviation was found between the experimental and calculated data in all cases, except for $b = 1$. Therefore, it was assumed that the adsorption reaction orders of C_3H_6 and O_2 are equal (with $b = 1$), so Eq. (15) was used. Principal component analysis gave the following result: first parameter group: eigenvector ($E: -0.996, S: -0.085, A: 0.000$), eigenvalue 62.50; second parameter group: eigenvector ($E: 0.084, S: -0.996, A: 0.000$), eigenvalue $1.68 \times$

10^{-1} ; third parameter group: eigenvector ($E: 0.000, S: 0.000, A: 0.999$), eigenvalue 2.94×10^{-5} . As with ethene, the result of the principal component analysis is that every parameter can be determined independently, but the calculated ignition temperature is not sensitive to the pre-exponential factor A_D .

The fitted parameters are $E_D(C_3H_6/Pt) = 161 \pm 53$ kJ/mol, $S_{C_3H_6,0}/S_{O_2,0} = 11.9 \pm 1.7$, and $A_D(C_3H_6/Pt) = (1.2 \pm 9.3) \times 10^{13} \text{ s}^{-1}$. The indicated errors are for 95% confidence limits. The fitted curve is shown by solid line in Fig. 2.

Assuming second-order adsorption of O_2 on polycrystalline Pt, the value of $b = 1$ means that the adsorption of propene on polycrystalline Pt is also of second order. The zero coverage sticking coefficient of O_2 on polycrystalline Pt was determined [9] to be $S_{O_2,0} = 0.024 \pm 0.004$. Therefore $S_{C_3H_6,0}/S_{O_2,0} = 11.9 \pm 1.7$ means the zero coverage sticking coefficient for C_3H_6 on polycrystalline Pt is $S_{C_3H_6,0} = 0.29 \pm 0.06$, where the 95% confidence limit reflects the propagation of errors.

6. Discussion

Equations (15) and (17) relate the ignition temperature to the composition of the gas, using parameters of the experimental setup and for the adsorption and desorption. These equations were used to determine parameters for the adsorption and desorption of ethene and propene on a polycrystalline platinum surface. In our treatment, the heat loss through the solid structure was neglected. This may introduce errors into the value determined for the pre-exponential factor; these errors depend on the ratio of the heat loss via the solid structure and the heat loss through

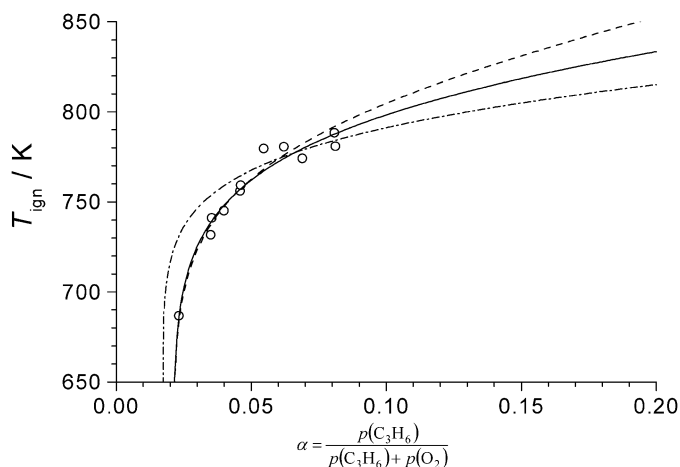


Fig. 2. Measured (circles) and calculated (lines) surface ignition temperature for the ignition of propene. The dashed line shows the result when the value of b was determined using Eq. (17). The final parameters were obtained assuming $b = 1$ and using Eq. (15) (solid line). The dash-dot line shows the ignition temperature as a function of composition, calculated using parameters $A_D = 10^{13} \text{ s}^{-1}$ and $E_D = 72.8 \text{ kJ mol}^{-1}$, as recommended by Tsai et al. [14].

the gas phase. We assume that before oxidation, the fuel does not decompose on the surface. Decomposition of the fuel before oxidation may cause further error in the pre-exponential factor. As has been shown in Section 2, if these constraints do not hold, the pre-exponential factor determined from fitting will be biased; however, the determination of the activation energy of desorption and the ratio of the sticking coefficients will not be affected.

6.1. Parameters for the adsorption and desorption of ethene

The parameters determined in this work are $E_D(\text{C}_2\text{H}_4/\text{Pt}) = 136 \pm 21 \text{ kJ/mol}$, $S_{\text{C}_2\text{H}_4,0}/S_{\text{O}_2,0} = 15.6 \pm 1.9$, and $A_D(\text{C}_2\text{H}_4/\text{Pt}) = (5.5 \pm 16.3) \times 10^{11} \text{ s}^{-1}$. The determined value of $b = 1$ means that the order for adsorption of ethene is equal to that for oxygen. Since the adsorption of oxygen is usually assumed to be second-order, the adsorption of ethene on polycrystalline Pt is also second-order. The zero coverage sticking coefficient for C_2H_4 on polycrystalline Pt is $S_{\text{C}_2\text{H}_4,0} = 0.38 \pm 0.08$.

Tsai et al. [14] measured a zero coverage sticking coefficient for C_2H_4 on Pt(111) of $S_{\text{C}_2\text{H}_4,0} = 1.0 \pm 0.1$ at 100 K and a “slightly lower” value at 150 K. No other measurement has been found in the literature. Wolf et al. [10] used $S_{\text{C}_2\text{H}_4,0} = 1.0$ in their model for the conversion of methane; however, ethene played only a marginal role in their work, and the origin of this value was not indicated.

The oxidation of ethene on a Pt(111) surface has been investigated [33,34], but no parameters for adsorption and desorption were determined. Zerkle et al. [11], dealing with the catalytic partial oxidation

of ethane, used a detailed reaction mechanism, also involving ethene as a product. They adjusted the parameters for the heterogeneous chemical mechanism to fit their measurements. They used $S_{\text{C}_2\text{H}_4,0} = 0.015$, which is lower than the value obtained in our work. However, Zerkle et al. [11] did not fit $S_{\text{C}_2\text{H}_4,0}$; it was only “adjusted within reasonable bounds, so that an approximate fit of the experimental data was achieved.” They also stated that the measurements they used could have been reproduced with different parameter sets as well.

For the activation energy of the desorption of ethene, Wolf et al. [10] used $E_D(\text{C}_2\text{H}_4/\text{Pt}) = 50.2 \text{ kJ/mol}$; however, the source of this value is not clear from their article. This value was also used by Zerkle et al. [11] in a description of the partial oxidation of ethane catalyzed by platinum at 1150–1250 K.

6.2. Parameters for the adsorption and desorption of propene

The estimated parameters are $E_D(\text{C}_3\text{H}_6/\text{Pt}) = 161 \pm 53 \text{ kJ/mol}$, $S_{\text{C}_3\text{H}_6,0}/S_{\text{O}_2,0} = 11.9 \pm 1.7$, and $A_D(\text{C}_3\text{H}_6/\text{Pt}) = (1.2 \pm 9.3) \times 10^{13} \text{ s}^{-1}$. The adsorption of propene on polycrystalline Pt is also second order. The zero coverage sticking coefficient for C_3H_6 on polycrystalline Pt was found to be $S_{\text{C}_3\text{H}_6,0} = 0.29 \pm 0.06$.

Tsai et al. [14] reported for C_3H_6 on Pt(111) that $S_{\text{C}_3\text{H}_6,0} = 1.0 \pm 0.05$ at 100–150 K. No other measured sticking coefficient for propene at higher temperatures or for polycrystalline Pt has been found in the literature.

Our method of calculating the ratios of sticking coefficients from ignition data have provided val-

ues of $S_{\text{H}_2,0}/S_{\text{O}_2,0}$, $S_{\text{CO},0}/S_{\text{O}_2,0}$, $S_{\text{O}_2,0}/S_{\text{CH}_4,0}$, $S_{\text{C}_2\text{H}_4,0}/S_{\text{O}_2,0}$, and $S_{\text{C}_3\text{H}_6,0}/S_{\text{O}_2,0}$. Using a single measured absolute sticking coefficient, $S_{\text{CO},0} = 1.0$, the following range of sticking coefficients (for zero coverage) on polycrystalline Pt were derived: $S_{\text{H}_2,0} = 0.88 \pm 0.40$, $S_{\text{C}_2\text{H}_4,0} = 0.38 \pm 0.08$, $S_{\text{C}_3\text{H}_6,0} = 0.29 \pm 0.06$, $S_{\text{O}_2,0} = 0.024 \pm 0.004$, and $S_{\text{CH}_4,0} = 0.0041 \pm 0.0009$. Our method has also provided the following activation energies for desorption: $E_{\text{D}}(\text{H}_2/\text{Pt}) = 43.3 \pm 5.2$ kJ/mol, $E_{\text{D}}(\text{CO}/\text{Pt}) = 107.2 \pm 12.7$ kJ/mol, $E_{\text{D}}(\text{C}_2\text{H}_4/\text{Pt}) = 136 \pm 21$ kJ/mol, $E_{\text{D}}(\text{C}_3\text{H}_6/\text{Pt}) = 161 \pm 53$ kJ/mol, $E_{\text{D}}(\text{O}_2/\text{Pt}) = 190 \pm 34$ kJ/mol. The order and also these values are in good accord with our present knowledge of the chemistry of adsorption.

Tsai et al. [14] measured the desorption of propene from Pt(111) using temperature programmed desorption (TPD). They estimated the activation energy for desorption to be 72.8 kJ/mol by taking the TPD peak at 284 K, assuming first order desorption kinetics and a pre-exponential factor of 10^{13} s^{-1} . As demonstrated in Fig. 2, the value of Tsai et al. [14] is not in agreement with the heterogeneous ignition data.

Chatterjee et al. [13] studied the oxidation of propene inside a single channel of a monolithic three-way catalyst, using a two-dimensional flow-field, coupled with a detailed surface reaction model. In this mechanism, the data of Tsai et al. [14] for A_{D} , E_{D} , and $S_{\text{C}_3\text{H}_6,0}$ were used. They found that the measured conversions of propene were not reproduced well. The values determined in our work may contribute to better agreement of the calculated and experimental results for monolithic three-way catalysts.

6.3. Uncertainty of the parameters

The sensitivity analysis shows that the fitting function is not sensitive to the value of the pre-exponential factor; therefore, its error limits are high. Furthermore, if the assumptions used do not apply, the fitted pre-exponential factor is biased. The uncertainty range of the pre-exponential factor determined in this work is too high, and its value may be considered to be correct only to an order of magnitude, so its use is not recommended.

On the other hand, the fitting function is very sensitive to the activation energy and the ratio of the sticking coefficients, and any violation of the simplifying assumptions does not introduce errors to their values. Therefore, the determined values of the activation energy for desorption and the ratio of the sticking coefficients can be assumed to be reliable.

6.4. Comparison with multistep mechanisms

Zerkle et al. [11] studied the partial oxidation of ethane using a detailed reaction mechanism and found

that experimental data could be reproduced with different parameter sets. This indicates that the parameters are coupled, so a determination of the individual parameters by fitting may be difficult. Wolf et al. [10] dealt with the simulation of oxygen-free methane conversion using a detailed reaction mechanism, which included ethene as well. However, because the oxidation reactions are missing, their detailed model cannot be directly used to study heterogeneous ignition. Chatterjee et al. [13] studied the oxidation of propene inside a monolithic three-way catalyst, and applied a detailed reaction mechanism, coupled with a calculation of the flow field. While it may be possible to use their model for the determination of unknown modeling parameters, their model requires considerable computational resources, and using it for fitting would be quite inconvenient.

7. Conclusions

A novel method has been presented for evaluating measurements of heterogeneous ignition temperatures for the oxidation of C_2H_4 and C_3H_6 on a polycrystalline platinum surface. This method [9] uses an analytical model based on 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 for the adsorption/desorption equilibria. 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 measured heterogeneous ignition temperatures and to obtain unknown physical parameters via nonlinear least squares fitting.

This new method was used to determine the activation energy for the desorption of C_2H_4 and C_3H_6 . In addition, the ratios of the zero coverage sticking coefficients $S_{\text{C}_2\text{H}_4,0}/S_{\text{O}_2,0}$ and $S_{\text{C}_3\text{H}_6,0}/S_{\text{O}_2,0}$, and the ratios of adsorption orders were also determined. Only an order of magnitude estimate can be given for the pre-exponential factor of desorption, because the ignition temperature is not sensitive to it. The parameters obtained for adsorption and desorption were tested by calculating ignition temperatures at different gas compositions and comparing them with the experimental data.

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References

- [1] P. Cho, C.K. Law, *Combust. Flame* 66 (2) (1986) 159–170.
- [2] A. Schwartz, L.L. Holbrook, H. Wise, *J. Catal.* 21 (1971) 199–207.
- [3] W.R. Patterson, C. Kernal, *J. Catal.* 2 (1963) 465–478.
- [4] W.R. Williams, M.T. Stenzel, X. Song, L.D. Schmidt, *Combust. Flame* 84 (3–4) (1991) 277–291.
- [5] G. Vesper, L.D. Schmidt, *AIChE J.* 42 (4) (1996) 1077–1087.
- [6] T.A. Griffin, L.D. Pfefferle, *AIChE J.* 36 (6) (1990) 861–870.
- [7] M. Ziauddin, G. Vesper, L.D. Schmidt, *Catal. Lett.* 46 (3–4) (1997) 159–167.
- [8] L. Hiam, H. Wise, S. Chaikin, *J. Catal.* 9 (1968) 272–276.
- [9] T. Perger, T. Kovács, T. Turányi, C. Treviño, *J. Phys. Chem. B* 107 (10) (2003) 2262–2274.
- [10] M. Wolf, O. Deutschmann, F. Behrendt, J. Warnatz, *Catal. Lett.* 61 (1999) 15–25.
- [11] D.K. Zerkle, M.D. Allendorf, M. Wolf, O. Deutschmann, *J. Catal.* 196 (2000) 18–39.
- [12] A.K. Avci, D.L. Trimm, A.E. Aksoylu, Z.I. Önsan, *Catal. Lett.* 88 (2003) 17–22.
- [13] D. Chatterjee, O. Deutschmann, J. Warnatz, *Faraday Discuss.* 119 (2001) 371–384.
- [14] Y.-L. Tsai, C. Xu, B.E. Koel, *Surf. Sci.* 385 (1) (1997) 37–59.
- [15] C. Treviño, *Combust. Theory Modelling* 3 (3) (1999) 469–477.
- [16] M. Rinnemo, O. Deutschmann, F. Behrendt, B. Kasemo, *Combust. Flame* 111 (4) (1997) 312–326.
- [17] M. Rinnemo, D. Kulginov, S. Johansson, K.L. Wong, V.P. Zhdanov, K. Kasemo, *Surf. Sci.* 376 (1–3) (1997) 297–309.
- [18] G. Vesper, M. Ziauddin, L.D. Schmidt, *Catal. Today* 47 (1999) 219–228.
- [19] L.C. Burmeister, *Convective Heat Transfer*, second ed., Wiley, New York, 1993.
- [20] D.A. Frank-Kamenetskii, *Diffusion and Heat Transfer in Chemical Kinetics*, second ed., Plenum Press, New York, 1969.
- [21] J. Warnatz, M.D. Allendorf, R.J. Kee, M.E. Coltrin, *Combust. Flame* 96 (4) (1994) 393–406.
- [22] C. Treviño, J.C. Prince, *Surf. Sci.* 449 (1–3) (2000) 61–74.
- [23] R.J. Kee, J.A. Miller, *A Structured Approach to the Computational Modeling of Chemical Kinetics and Molecular Transport in Flowing Systems*, SAND86-8841, Sandia National Laboratories Report, 1992.
- [24] E. Keszei, P. Holpár, A subroutine to perform multiple nonlinear parameter estimation, available at: <http://femto.chem.elte.hu/fit/englishprog.htm>.
- [25] S. Vajda, P. Valkó, T. Turányi, *Int. J. Chem. Kinet.* 17 (1) (1985) 55–81.
- [26] T. Turányi, *Comput. Chem.* 14 (3) (1990) 253–254.
- [27] Y.K. Park, P. Aghalayam, D.G. Vlachos, *J. Phys. Chem. A* 103 (40) (1999) 8101–8107.
- [28] P.-A. Bui, D.G. Vlachos, P.R. Westmoreland, *Ind. Eng. Chem. Res.* 36 (7) (1997) 2558–2567.
- [29] P. Aghalayam, Y.K. Park, D.G. Vlachos, *Proc. Combust. Inst.* 28 (2000) 1331–1339.
- [30] G. Vesper, J. Frauhammer, L.D. Schmidt, G. Eigenberger, *Stud. Surf. Sci. Catal.* 109 (1997) 273–284.
- [31] B. Helling, B. Kasemo, V.P. Zhdanov, *J. Catal.* 132 (1991) 210–228.
- [32] D.M. Collins, J.B. Lee, W.E. Spicer, *Surf. Sci.* 55 (2) (1976) 389–402.
- [33] H. Arnolds, *Surf. Sci.* 548 (2004) 151–156.
- [34] H. Steininger, H. Ibach, S. Lehwald, *Surf. Sci.* 117 (1982) 685–698.