

# Determination of Adsorption and Desorption Parameters from Ignition Temperature Measurements in Catalytic Combustion Systems

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When a cold catalyst is exposed to a fuel-oxygen mixture, the surface gets covered with the more effectively adsorbing species. When the temperature is increased, this species is desorbed and the ignition temperature is determined by the rate of desorption. Based on the equations for the heat balance, expressions were derived for the calculation of ignition temperature from the parameters of the experimental setup, the preexponential factor  $A_d$  and activation energy  $E_d$  of desorption, the ratio of sticking coefficients, and the ratio of adsorption orders of fuel and oxygen. Published experimental data for the catalytic ignition of CO, H<sub>2</sub>, and CH<sub>4</sub> were reinterpreted using the expressions obtained, and the following parameters were determined for polycrystalline platinum catalyst:  $E_d(\text{H}_2/\text{Pt}) = 43.3 \pm 5.2$  kJ/mol,  $E_d(\text{CO}/\text{Pt}) = 107.2 \pm 12.7$  kJ/mol,  $E_d(\text{O}_2/\text{Pt}) = 190 \pm 34$  kJ/mol,  $S_{\text{H}_2,0}/S_{\text{O}_2,0} = 36.7 \pm 9.6$ ,  $S_{\text{CO},0}/S_{\text{O}_2,0} = 41.2 \pm 8.5$ ,  $S_{\text{O}_2,0}/S_{\text{CH}_4,0} = 5.9 \pm 0.3$ . Error limits refer to a confidence level of 0.95. The activation energy of desorption for CO and O<sub>2</sub> and the ratio of zero coverage sticking coefficients of O<sub>2</sub> and CH<sub>4</sub> are the first experimentally based determinations of these parameters. Experimental ignition temperatures could be reproduced assuming second-order adsorption of CO, H<sub>2</sub>, and O<sub>2</sub> on the Pt surface. These reaction orders have been debated in the literature.

## 1. Introduction

Homogeneous gas-phase combustion has the capability of the production of a significant amount of energy in a small volume but on the expense of high NO<sub>x</sub> and other pollutant formation. Reaction of fuel and oxygen on a catalyst surface, called heterogeneous combustion, has the advantage of low NO<sub>x</sub> and other pollutant generation, but in this case, the reaction rates are much lower. A new technique is the catalytically stabilized thermal (CST) combustion, where the gas phase combustion is initiated and stabilized by a catalytically active surface.<sup>1</sup> The presence of catalyst extends the stable burner operation to leaner mixtures and therefore lowers operating temperatures. In CST combustors, the reaction rates are high, but pollutant formation is near zero. Other practically important applications of heterogeneous combustion include car exhaust catalysis, catalytic afterburning in chemical reactors, radiant heaters, chemical reactor heaters, and catalytic combustors for gas turbine applications.<sup>2</sup>

Design of heterogeneous combustors and catalytically stabilized burners requires the proper quantitative description of heterogeneous ignition and combustion. Several papers were published in the last 10 years on the experimental study of heterogeneous ignition. In accordance with the great theoretical and practical importance of this field, a large number of papers was published on numerical modeling of heterogeneous combustion and very good agreement with the experimental data was found.<sup>3–5</sup> However, all models contain many uncertain and therefore tuneable parameters. As an example, similar ignition

temperature–gas composition curves could be calculated using very different parameter sets.<sup>6</sup>

The aim of this paper is to present a general method for the determination of the most critical parameters for heterogeneous ignition from ignition temperature measurements. Using this method, the activation energy of desorption and ratio of sticking coefficients of reactants can be determined from experimental ignition temperature data. In sections 2–4, expressions are derived that relate ignition temperature to experimental and physical constants and parameters of adsorption and desorption. In section 5, the obtained equations are compared with previous studies on heterogeneous ignition. In section 6, previously published experimental data for the catalytic ignition of CO, H<sub>2</sub>, and CH<sub>4</sub> are reinterpreted using these equations, and the activation energy of desorption and the ratio of sticking coefficients of fuel and oxygen are determined. The values obtained are compared with direct experimental determinations of these values, if available.

## 2. Heat Balance in Catalytic Ignition

In catalytic ignition experiments, the catalyst is usually a Pt plate or Pt wire. In stagnation point flow experiments, the laminar flow of the fuel/oxygen/diluent gas mixture is perpendicular toward a platinum plate.<sup>7</sup> In another type of experimental arrangement, a catalytic wire is placed vertically in a stagnating gas<sup>6</sup> or in a cross-stream gas flow.<sup>6,8,9</sup> In both types of experiments, the 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. Because of the exothermic chemical reaction

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and the external heating, temperature  $T$  of the surface of the catalyst is always higher than temperature  $T_\infty$  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. Because of 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,<sup>10</sup> convective heat loss depends linearly on the difference of temperature  $T$  of the surface and temperature  $T_\infty$  of the gas far from the surface and is proportional to the ratio of the heat conductivity  $\lambda$  of the gas and the characteristic thermal length  $L_c$ :

$$\omega \Delta_r H + Q_e = \frac{\lambda}{L_c} (T - T_\infty) \quad (1)$$

Here  $\Delta_r H$  is the enthalpy of the overall reaction,  $\omega$  is the rate of the overall reaction, and  $Q_e$  is the rate of heat production due to electric heating. The thickness of the thermal boundary layer  $L_c$  can be calculated from the flow geometry.<sup>10</sup> For stagnation point flow configurations

$$L_c = 2 \times 10^{-2} \sqrt{\nu/a} \quad (2)$$

where  $\nu$  is the kinematic viscosity of the gas at temperature  $T_\infty$  and  $a$  is the velocity gradient of the gas flow. Units of  $L_c$ ,  $\nu$ , and  $a$  are m,  $\text{m}^2 \text{s}^{-1}$ , and  $\text{s}^{-1}$ , respectively. If a wire of diameter  $d$  is placed perpendicularly in a flow of velocity  $u$ , the width of the equivalent characteristic thickness is

$$L_c = \frac{d}{0.891 \times 10^2 Re^{0.33}} \quad (3)$$

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

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. (See Figure 2 in ref 11.) 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 because of the chemical reactions, without additional heating:

$$\frac{\partial T}{\partial Q_e} \rightarrow \infty \quad \text{or} \quad \frac{\partial Q_e}{\partial T} = 0 \quad (4)$$

According to the Frank-Kamenetskii condition,<sup>12</sup> differentiating eq 1 with respect to the temperature results in an expression for the condition of ignition:

$$\frac{\partial \omega}{\partial T} \Delta_r H + \frac{\partial Q_e}{\partial T} = \frac{\lambda}{L_c} \quad (5)$$

According to eq 4, at the ignition temperature  $T$ , the time derivative of  $Q_e$  is zero and the following equation becomes the condition of heterogeneous ignition

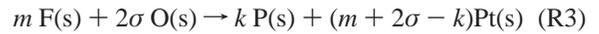
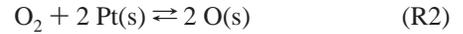
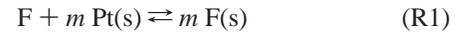
$$\frac{\partial \omega}{\partial T} \Delta_r H = \frac{\lambda}{L_c} \quad (6)$$

### 3. Rate of the Overall Reaction

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



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:<sup>13</sup>



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.

**3.1. Rates of the Surface Reactions.** The change of the surface coverage of species F(s) and O(s) during the reaction can be described by the following system of differential equations:

$$\frac{d\theta_F}{dt} = mr_{F,A} - mr_{F,D} - \frac{\omega_F}{\Gamma} \quad (8)$$

$$\frac{d\theta_O}{dt} = 2r_{O,A} - 2r_{O,D} - \frac{\omega_O}{\Gamma} \quad (9)$$

where  $\theta_F$  and  $\theta_O$  are the surface coverage of fuel and oxygen, respectively;  $r_{F,A}$ ,  $r_{O,A}$ ,  $r_{F,D}$ , and  $r_{O,D}$  denote the adsorption rate of fuel and oxygen and the desorption rate of fuel and oxygen, respectively.  $\omega_F$  and  $\omega_O$  are the consumption rate of fuel and oxygen in the overall chemical reaction, respectively;  $\Gamma$  is the density of active sites on the surface of the catalyst. In the case of Pt catalyst, site density is  $\Gamma = 2.707 \times 10^{-5} \text{ mol m}^{-2}$ .<sup>14</sup> The analysis does not consider inhomogeneity but takes only into account an effective mean value of the concentration of surface species.

In stationary state  $d\theta_F/dt = 0$  and  $d\theta_O/dt = 0$ , and therefore,  $\omega_F$  and  $\omega_O$  can be expressed from eqs 8 and 9, respectively:

$$\omega_F = (mr_{F,A} - mr_{F,D})\Gamma \quad (10)$$

$$\omega_O = (2r_{O,A} - 2r_{O,D})\Gamma \quad (11)$$

The stoichiometry of reaction step R3 makes a relation between consumption rates  $\omega_F$  and  $\omega_O$ :

$$\omega_F = \frac{m}{2\sigma} \omega_O \quad (12)$$

The overall reaction rate  $\omega$  can be obtained from the stoichiometry of reaction step R1 or R2:

$$\omega = \frac{\omega_F}{m} = \frac{\omega_O}{2\sigma} \quad (13)$$

$$\omega = (r_{F,A} - r_{F,D})\Gamma = (r_{O,A} - r_{O,D})\frac{\Gamma}{\sigma} \quad (14)$$

The rate of adsorption of species  $i$  is proportional to the number of species hitting the surface:<sup>15</sup>

$$r_{i,A} = \frac{S_i p X_i}{\Gamma \sqrt{2\pi W_i RT}} = \frac{S_i p_i}{\Gamma \sqrt{2\pi W_i RT}} \quad (15)$$

where  $p$  is the pressure of the gas mixture;  $W_i$ ,  $X_i$ , and  $p_i$  are the molar mass, the mole fraction, and the partial pressure of species  $i$  in the gas phase, respectively;  $S_i$  is the sticking coefficient of species  $i$  belonging to the actual coverage.  $S_i$  can be a nontrivial function of the ratio of vacant sites and may depend on which species cover the surface. However,  $S_i$  can approximately be related to the zero coverage sticking coefficient  $S_{i,0}$  by the following power-law expression (see, e.g., ref 5):

$$S_i = S_{i,0} \theta_v^{n_{i,A}} \quad (16)$$

where  $n_{i,A}$  is the reaction order of adsorption of species  $i$  and  $\theta_v$  is the coverage of vacant sites. Substituting eq 16 into eq 15 yields

$$r_{i,A} = \frac{S_{i,0} p X_i}{\Gamma \sqrt{2\pi W_i RT}} \theta_v^{n_{i,A}} = \frac{S_{i,0} p_i}{\Gamma \sqrt{2\pi W_i RT}} \theta_v^{n_{i,A}} = k_{i,A} \theta_v^{n_{i,A}} \quad (17)$$

where  $k_{i,A} = S_{i,0} p X_i / [\Gamma \sqrt{2\pi W_i RT}]^{1/2}$  is the rate of adsorption of species  $i$  at zero surface coverage.

Denoting the reaction order of desorption of species  $i$  by  $n_{i,D}$ , the following expression can be obtained for the rate of desorption:

$$r_{i,D} = k_{i,D} \theta_i^{n_{i,D}} \quad (18)$$

In this equation  $k_{i,D}$  denotes the rate coefficient of desorption of species  $i$ , which depends on temperature by an Arrhenius type expression:

$$k_{i,D} = A_{i,D} \exp(-E_{i,D}/RT) \quad (19)$$

Therefore, the rate of desorption is described by the following expression:

$$r_{i,D} = \theta_i^{n_{i,D}} A_{i,D} \exp(-E_{i,D}/RT) \quad (20)$$

From eqs 14, 17, and 18, the following equation can be obtained for the relation between the adsorption–desorption parameters of the fuel and oxygen and the overall reaction rate:

$$\frac{\omega}{\Gamma} = k_{F,A} \theta_v^{n_{F,A}} - k_{F,D} \theta_F^{n_{F,D}} = \frac{1}{\sigma} (k_{O,A} \theta_v^{n_{O,A}} - k_{O,D} \theta_O^{n_{O,D}}) \quad (21)$$

Note that in eqs 18–20, preexponential factor  $A_{i,D}$  was expressed with surface coverages and not with surface concentrations. To convert it to the preexponential factor  $A'_{i,D}$  expressed with surface concentrations, it has to be divided with the appropriate power of the surface site density:

$$A'_{i,D} = \frac{A_{i,D}}{\Gamma^{n_{i,D}-1}} \quad (22)$$

**3.2. Surface Coverage before Ignition.** Exposing a bare catalyst surface to a mixture of fuel and oxygen gases below the ignition temperature, the surface becomes covered by both fuel and oxygen atom species. Depending on the conditions, either the fuel or the oxygen has a higher coverage. If the fuel has initially a higher coverage, all oxygen atoms bound to the surface are consumed soon by surface reactions. The vacant sites will be also covered mainly by fuel species, and the oxygen atoms adsorbed will be also fully consumed. Therefore, in a

few such steps, the surface becomes almost fully covered by fuel species. In this case, increasing the concentration of fuel in the mixture, the mixture becomes less reactive and ignition happens only at higher temperature. This means that increasing the fuel/oxygen ratio in the gas mixture will increase the ignition temperature. The  $H_2/O_2/Pt$ ,<sup>8</sup>  $CO/O_2/Pt$ ,<sup>8</sup> ethylene/ $O_2/Pt$ ,<sup>8</sup> propylene/ $O_2/Pt$ ,<sup>8</sup> and  $NH_3/O_2/Pt$ <sup>16</sup> systems show such behavior. In the opposite case, the surface is initially almost fully covered with oxygen atoms, and the increasing fuel/oxygen ratio decreases the ignition temperature. Such systems are the  $CH_4/O_2/Pt$ ,<sup>16–18</sup>  $C_2H_6/O_2/Pt$ ,<sup>17,19</sup> propane/ $O_2/Pt$ ,<sup>8,16,18,20</sup> and butane/ $O_2/Pt$ <sup>8,20</sup> systems. In the case of some fuels, like ethane and isobutane, the ignition temperature decreases as a function of increasing fuel/oxygen ratio at lean ( $\varphi < 1$ ), stoichiometric ( $\varphi = 1$ ), and moderately rich ( $1 < \varphi < 4$ ) conditions but starts to increase at very fuel rich ( $\varphi > 4$ ) conditions,<sup>18</sup> indicating a change from initial oxygen coverage to initial fuel coverage regime. A more detailed description of the condition for full initial fuel or oxygen coverage is given in the Appendix.

In the following sections, expressions for the rate of overall reaction will be deduced and equations for the relation of adsorption–desorption parameters and ignition temperature will be produced. These equations depend on the type of initial coverage and the order of adsorption reactions.

**3.3. Initial Fuel Coverage.** 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 ( $\theta_v \ll 1$ ). Therefore, eq 21 can be simplified to

$$\omega = \frac{\Gamma}{\sigma} k_{O,A} \theta_v^{n_{O,A}} \quad (23)$$

The ratio  $k_{F,D}/k_{F,A}$  can also be expressed from eq 21:

$$k_{F,A} \theta_v^{n_{F,A}} - k_{F,D} = \frac{k_{O,A} \theta_v^{n_{O,A}}}{\sigma} \quad (24)$$

$$\frac{k_{F,D}}{k_{F,A}} = \theta_v^{n_{F,A}} - \frac{k_{O,A}}{\sigma k_{F,A}} \theta_v^{n_{O,A}} \quad (25)$$

$$\frac{k_{F,D}}{k_{F,A}} = \theta_v^{n_{F,A}} \left( 1 - \frac{k_{O,A}}{\sigma k_{F,A}} \theta_v^{n_{O,A}-n_{F,A}} \right) \quad (26)$$

Three different cases can be distinguished, depending on the reaction orders of the adsorption of reactants: when the orders are equal ( $n_{F,A} = n_{O,A}$ ), when the order of adsorption of oxygen is larger ( $n_{F,A} < n_{O,A}$ ), and when the order of adsorption of the fuel is larger ( $n_{F,A} > n_{O,A}$ ).

**3.3.1. Case 1:**  $n_{F,A} = n_{O,A}$ . If the order of adsorption of the fuel  $n_{F,A}$  is equal to the order of adsorption of oxygen  $n_{O,A}$ , then  $n_{O,A} - n_{F,A} = 0$ ,  $\theta_v^{n_{O,A}-n_{F,A}} = 1$  and eq 26 can be simplified to

$$\frac{k_{F,D}}{k_{F,A}} = \theta_v^{n_{F,A}} \left( 1 - \frac{k_{O,A}}{\sigma k_{F,A}} \right) \quad (27)$$

This allows the estimation of the ratio of the vacant sites:

$$\theta_v = \left( \frac{k_{F,D}}{k_{F,A}} \right)^{1/n_{F,A}} \left( 1 - \frac{k_{O,A}}{\sigma k_{F,A}} \right)^{-1/n_{F,A}} \quad (28)$$

Using eqs 23 and 28, the reaction rate is

$$\omega = \frac{\Gamma}{\sigma} k_{O,A} \left( \frac{k_{F,D}}{k_{F,A}} \right)^{n_{O,A}/n_{F,A}} \left( 1 - \frac{k_{O,A}}{\sigma k_{F,A}} \right)^{-n_{O,A}/n_{F,A}} \quad (29)$$

Because  $n_{O,A}/n_{F,A} = 1$ , therefore, the overall reaction rate is

$$\omega = \frac{\Gamma k_{F,D} k_{O,A}}{\sigma k_{F,A} - k_{O,A}} = \frac{\Gamma k_{F,D}}{\sigma \frac{k_{F,A}}{k_{O,A}} - 1} \quad (30)$$

3.3.2. Case 2:  $n_{F,A} < n_{O,A}$ . In eq 26,  $\theta_v \ll 1$ , and  $n_{O,A} - n_{F,A} > 0$ ; therefore,  $\theta_v^{n_{O,A}-n_{F,A}} \approx 0$ . The value of  $k_{O,A}/\sigma k_{F,A}$  is of the order of 1; thus, the second term in the parentheses can be neglected, resulting in the following expression:

$$\theta_v = \left( \frac{k_{F,D}}{k_{F,A}} \right)^{1/n_{F,A}} \quad (31)$$

Substituting the above expression into eq 23, the overall reaction rate can be estimated with the following term:

$$\omega = \frac{\Gamma k_{O,A} (k_{F,D})^{n_{O,A}/n_{F,A}}}{\sigma (k_{F,A})} \quad (32)$$

3.3.3. Case 3:  $n_{F,A} > n_{O,A}$ . This case is not possible if the surface is initially almost fully covered with the fuel. The justification is given in the Appendix.

**3.4. Initial Oxygen Coverage.** If initially the dominant surface species is oxygen ( $\theta_O \approx 1$ ), then the coverage of the fuel species is negligible ( $\theta_F \approx 0$ ) and the ratio of vacant sites is very small ( $\theta_v \ll 1$ ). Applying these simplifications to eq 21 yields

$$\omega = \Gamma k_{F,A} \theta_v^{n_{F,A}} \quad (33)$$

The ratio  $k_{O,D}/k_{O,A}$  can also be expressed from eq 12:

$$\sigma k_{F,A} \theta_v^{n_{F,A}} = k_{O,A} \theta_v^{n_{O,A}} - k_{O,D} \quad (34)$$

$$\frac{k_{O,D}}{k_{O,A}} = \theta_v^{n_{O,A}} - \sigma \frac{k_{F,A}}{k_{O,A}} \theta_v^{n_{F,A}} \quad (35)$$

$$\frac{k_{O,D}}{k_{O,A}} = \theta_v^{n_{O,A}} \left( 1 - \sigma \frac{k_{F,A}}{k_{O,A}} \theta_v^{n_{F,A}-n_{O,A}} \right) \quad (36)$$

Similarly to eq 26, three different cases can be distinguished, depending on the ratio of reaction orders of the adsorption of reactants.

3.4.1. Case 1:  $n_{F,A} = n_{O,A}$ . If the order of adsorption of the fuel  $n_{F,A}$  is equal to the order of adsorption of oxygen  $n_{O,A}$ , then  $n_{F,A} - n_{O,A} = 0$ ,  $\theta_v^{n_{F,A}-n_{O,A}} = 1$ , and eq 36 can be rearranged to

$$\frac{k_{O,D}}{k_{O,A}} = \theta_v^{n_{O,A}} \left( 1 - \sigma \frac{k_{F,A}}{k_{O,A}} \right) \quad (37)$$

This allows the estimation of the ratio of the vacant sites on the surface:

$$\theta_v = \left( \frac{k_{O,D}}{k_{O,A}} \right)^{1/n_{O,A}} \left( 1 - \sigma \frac{k_{F,A}}{k_{O,A}} \right)^{-1/n_{O,A}} \quad (38)$$

Using eqs 33 and 38, reaction rate  $\omega$  is

$$\omega = \Gamma k_{F,A} \left( \frac{k_{O,D}}{k_{O,A}} \right)^{n_{F,A}/n_{O,A}} \left( 1 - \sigma \frac{k_{F,A}}{k_{O,A}} \right)^{-n_{F,A}/n_{O,A}} \quad (39)$$

Because the reaction orders of adsorption are equal ( $n_{F,A}/n_{O,A} = 1$ ), the overall reaction rate is

$$\omega = \frac{\Gamma k_{O,D} k_{F,A}}{k_{O,A} - \sigma k_{F,A}} = \frac{\Gamma k_{O,D}}{\frac{k_{O,A}}{k_{F,A}} - \sigma} \quad (40)$$

3.4.2. Case 2:  $n_{F,A} > n_{O,A}$ . In eq 36, the number of vacant sites is very small ( $\theta_v \ll 1$ ), and the adsorption order of the fuel is greater than the order of the oxygen species ( $n_{F,A} - n_{O,A} > 0$ ); therefore,  $\theta_v^{n_{F,A}-n_{O,A}} \approx 0$ . The value of  $\sigma k_{F,A}/k_{O,A}$  is of the order of 1; thus, the second term in the parenthesis can be neglected, resulting in the following expression:

$$\theta_v = \left( \frac{k_{O,D}}{k_{O,A}} \right)^{1/n_{O,A}} \quad (41)$$

Substitution of this equation into eq 33 gives the following expression for the overall reaction rate:

$$\omega = \Gamma k_{F,A} \left( \frac{k_{O,D}}{k_{O,A}} \right)^{n_{F,A}/n_{O,A}} \quad (42)$$

3.4.3. Case 3:  $n_{F,A} < n_{O,A}$ . As it is discussed in the Appendix, this case is not possible if the surface is initially covered with oxygen.

#### 4. Condition of Ignition

Conditions of heterogeneous ignition for the various cases can be obtained by substituting the corresponding equations for reaction rates into eq 6.

**4.1. Initial Fuel Coverage, Case 1:  $n_{F,A} = n_{O,A}$ .** From eqs 6 and 30

$$\frac{\partial}{\partial T} \left( \frac{\Gamma k_{F,D}}{\sigma \frac{k_{F,A}}{k_{O,A}} - 1} \right) \Delta_r H = \frac{\lambda}{L_c} \quad (43)$$

This expression can be rewritten using eqs 17 and 19

$$\frac{\partial}{\partial T} \left( \frac{\Gamma A_{F,D} \exp(-E_{F,D}/RT)}{\sigma \frac{S_{F,0}}{S_{O,0}} \frac{X_F}{X_O} \sqrt{\frac{W_O}{W_F}} - 1} \right) \Delta_r H = \frac{\lambda}{L_c} \quad (44)$$

Ratio of zero coverage sticking coefficients has only weak temperature dependence; thus, the denominator on the left-hand side is nearly independent of temperature. Differentiation gives the following equation:

$$\frac{\Gamma A_{F,D} E_{F,D} \exp(-E_{F,D}/RT)}{RT^2} \Delta_r H = \frac{\lambda}{L_c} \left( \frac{S_{F,0}}{S_{O,0}} \frac{X_F}{X_O} \sqrt{\frac{W_O}{W_F}} - 1 \right) \quad (45)$$

Rearranging this expression, the following condition of ignition is obtained:

$$\frac{\Gamma \Delta_I H L_c A_{F,D} E_{F,D} \exp(-E_{F,D}/RT)}{\lambda RT^2 \left( \sigma \frac{X_F}{X_O} \sqrt{\frac{W_O}{W_F} \frac{S_{F,0}}{S_{O,0}}} - 1 \right)} = 1 \quad (46)$$

The kind of quantity calculated on the left-hand-side of this equation is usually called the ignition Damköhler number  $\Delta_I$ . In eq 46, 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 eq 46. 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.

**4.2. Initial Fuel Coverage, Case 2:  $n_{F,A} < n_{O,A}$ .** Substituting eq 32 into eq 6 results in the following expression:

$$\frac{\partial \omega}{\partial T} \Delta_I H = \frac{\partial}{\partial T} \left[ \frac{\Gamma k_{O,A} (k_{F,D})^{n_{O,A}/n_{F,A}}}{\sigma (k_{F,A})} \right] \Delta_I H = \frac{\partial}{\partial T} \left[ \frac{\Gamma k_{O,A} k_{F,D}^b}{\sigma k_{F,A}^b} \right] \Delta_I H = \frac{\lambda}{L_c} \quad (47)$$

where  $b = n_{O,A}/n_{F,A}$  denotes the ratio of the adsorption orders. Temperature dependence of parameters  $k_{O,A}$ ,  $k_{F,A}$ , and  $k_{F,D}$  have to be taken into account at the differentiation:

$$\frac{\partial \omega}{\partial T} = \frac{\Gamma}{\sigma} \left[ \left( \frac{\partial k_{O,A}}{\partial T} k_{F,A}^{-b} - k_{O,A} b k_{F,A}^{-b-1} \frac{\partial k_{F,A}}{\partial T} \right) k_{F,D}^b + \frac{k_{O,A} b k_{F,D}^{b-1} \frac{\partial k_{F,D}}{\partial T}}{k_{F,A}^b} \right] \quad (48)$$

Derivatives of  $k_{O,A}$ ,  $k_{F,A}$ , and  $k_{F,D}$  with respect to temperature can be obtained from eqs 17 and 19

$$\frac{\partial k_{F,A}}{\partial T} = \frac{-k_{F,A}}{2T} \quad (49)$$

$$\frac{\partial k_{O,A}}{\partial T} = \frac{-k_{O,A}}{2T} \quad (50)$$

$$\frac{\partial k_{F,D}}{\partial T} = \frac{k_{F,D} E_{F,D}}{RT^2} \quad (51)$$

Thus, eq 48 can be simplified to the following form:

$$\frac{\partial \omega}{\partial T} = \frac{\Gamma}{\sigma} \frac{k_{O,A} k_{F,D}^b}{k_{F,A}^b} \left( \frac{b-1}{2T} + b \frac{E_{F,D}}{RT^2} \right) \quad (52)$$

Starting from eq 47, and using the expression (52), (17), and (19) for  $k_{O,A}$ ,  $k_{F,A}$ , and  $k_{F,D}$ , respectively, results in the following equation:

$$\frac{\Delta_I H L_c \Gamma}{\lambda \sigma} \left( \frac{S_{O,0} A_{F,D}^b}{S_{F,0}^b} \right) \left( \frac{\Gamma \sqrt{2\pi RT}}{p} \right)^{b-1} \frac{X_O \sqrt{W_O}}{(X_F \sqrt{W_F})^b} \left( \frac{b-1}{2T} + b \frac{E_{F,D}}{RT^2} \right) \exp\left(\frac{-bE_{F,D}}{RT}\right) = 1 \quad (53)$$

Using eq 53, the 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 the ratio  $b$  of the adsorption reaction orders is known,  $E_{F,D}$  and  $A^* = S_{O,0} A_{F,D}^b / S_{F,0}^b$  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.

**4.3. Initial Oxygen Coverage, Case 1:  $n_{F,A} = n_{O,A}$ .** Combination of eqs 6 and 40 provides

$$\frac{\partial}{\partial T} \left( \frac{\Gamma k_{O,D}}{k_{F,A} - \sigma} \right) \Delta_I H = \frac{\lambda}{L_c} \quad (54)$$

Applying steps similar to the case of initial fuel coverage, the following equation can be derived:

$$\frac{\Gamma \Delta_I H L_c A_{O,D} E_{O,D} \exp(-E_{O,D}/RT)}{\lambda RT^2 \left( \frac{X_O}{X_F} \sqrt{\frac{W_F}{W_O} \frac{S_{O,0}}{S_{F,0}}} - \sigma \right)} = 1 \quad (55)$$

Desorption and adsorption parameters  $A_{O,D}$ ,  $E_{O,D}$ , and  $S_{O,0}/S_{F,0}$ , can be determined by nonlinear least-squares fitting from the measured gas composition–ignition temperature data pairs.

**4.4. Initial Oxygen Coverage, Case 2:  $n_{F,A} > n_{O,A}$ .** Based on eq 42, the temperature derivative of the overall reaction rate  $\omega$  can be rearranged to

$$\frac{\partial \omega}{\partial T} = \frac{\partial}{\partial T} \left[ \Gamma k_{F,A} \left( \frac{k_{O,D}}{k_{O,A}} \right)^{n_{F,A}/n_{O,A}} \right] = \frac{\partial}{\partial T} \left[ \Gamma \frac{k_{F,A} k_{O,D}^{1/b}}{k_{O,A}^{1/b}} \right] \quad (56)$$

where  $b = n_{O,A}/n_{F,A}$  denotes the ratio of the adsorption orders. After differentiation

$$\frac{\partial \omega}{\partial T} = \Gamma \left[ \left( \frac{\partial k_{F,A}}{\partial T} k_{O,A}^{-1/b} - k_{F,A} b^{-1} k_{O,A}^{-1/b-1} \frac{\partial k_{O,A}}{\partial T} \right) k_{O,D}^{1/b} + \frac{k_{F,A}}{k_{O,A}^{1/b}} \frac{1}{b} k_{O,D}^{1/b-1} \frac{\partial k_{O,D}}{\partial T} \right] \quad (57)$$

Using the differentials (49)–(51), the following expression is obtained:

$$\frac{\partial \omega}{\partial T} = \Gamma \frac{k_{F,A} k_{O,D}^{1/b}}{k_{O,A}^{1/b}} \left( \frac{1/b-1}{2T} + 1/b \frac{E_{O,D}}{RT^2} \right) \quad (58)$$

Substitution of eqs 17, 19, and 58 into eq 6 results in the following equation:

$$\frac{\Delta_I H L_c \Gamma}{\lambda} \left( \frac{S_{F,0} A_{O,D}^{1/b}}{S_{O,0}^{1/b}} \right) \left( \frac{\Gamma \sqrt{2\pi RT}}{p} \right)^{1/b-1} \frac{X_F \sqrt{W_F}}{(X_O \sqrt{W_O})^{1/b}} \left( \frac{1/b-1}{2T} + 1/b \frac{E_{O,D}}{RT^2} \right) \exp\left(\frac{-E_{O,D}}{bRT}\right) = 1 \quad (59)$$

Again, this equation can be used for the calculation of ignition temperature if all data are known or for the determination of unknown parameters from the experimental data.

Similarly to eq 46, the left-hand-sides of eqs 53, 55, and 59 calculate quantities that are called Damköhler number of ignition.

## 5. Comparison with Previous Studies on Heterogeneous Ignition

The qualitative meaning of eqs 46, 53, 55, and 59 is that the ignition temperature depends on the parameters of the experi-

ment, like experimental geometry and heat conductivity of gases, and also depends on parameters of the reaction system, like enthalpy of the reaction, ratio of zero coverage sticking coefficients, and the desorption Arrhenius parameter of the species that covers the surface initially. It might be surprising that ignition temperature is completely independent of the rate parameters of surface reactions. This result is in agreement with the sensitivity analysis results of Vlachos and Westmoreland.<sup>21</sup> They modeled catalytic ignition of H<sub>2</sub>/air mixtures over platinum with detailed transport, gas-phase, and surface kinetics and found that catalytic ignition temperature is sensitive to the rate of competitive dissociative adsorption of H<sub>2</sub> and O<sub>2</sub> and the desorption of H(s). Bui et al.<sup>22</sup> did a similar sensitivity study on surface ignition of methane/oxygen/air mixtures and also found that dissociative adsorption of molecular oxygen and the decomposition of methane on the surface are the most important steps in affecting ignition. Deutschmann et al.<sup>3</sup> studied the catalytic ignition of H<sub>2</sub>, CO, and CH<sub>4</sub>. They stated that “a prerequisite for catalytic ignition is the availability of a sufficient number of uncovered surface sites” and that kinetic data for adsorption and desorption are critical for the ignition process.

There are several theoretical studies on catalytic ignition in the literature. These include modeling of the chemical reactions using detailed surface and gas-phase kinetics,<sup>3,6,7,14,23</sup> detailed gas-phase kinetics coupled with one-step surface reaction,<sup>24</sup> one-step surface reaction only,<sup>13,15,25–27</sup> or steady-state approximation for surface reactions.<sup>28–30</sup> Some authors used the wire in flow geometry,<sup>6,23,25,27,28</sup> and others considered stagnation flow configuration.<sup>3,7,13–15,23,24,26,30</sup> In some cases, authors used experimentally determined values for the adsorption and desorption parameters, and in other cases, theoretically approximated values were used. In these studies, the predicted ignition temperature vs equivalence ratio functions were usually more or less in accordance with the experimental data. The determination of adsorption and desorption parameters was not attempted from the experimental data in any of these articles.

## 6. Interpretation of Experimental Heterogeneous Ignition Data

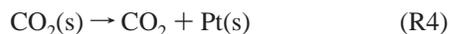
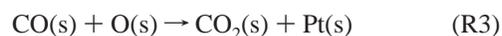
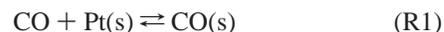
We have found more than 50 publications dealing with heterogeneous ignition. Most of these articles were published in the past decade, indicating a significant interest in this field. However, only one dozen articles report experimental ignition temperature measurements. In the following sections, a part of these experimental data are reanalyzed using the analytical expressions derived on the dependence of ignition temperature from experimental and physical parameters.

In all cases, the experimental data were digitized from the original publications, and the experimental conditions were extracted from the text of the article. The utility programs of the CHEMKIN-II package<sup>31</sup> were used for the calculation of parameters such as thermal conductivity and viscosity of gas mixtures at a given temperature. Knowing the experimental conditions, eqs 46, 53, 55, and 59 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.

An important question is if the parameters to be determined are effective and/or independent of each other. Principal component analysis<sup>32</sup> of local sensitivity matrix is an efficient method to answer such type of questions. The local sensitivity

matrix  $S = \{\partial Y_i / \partial p_k\}$  shows the effect of a small change in parameter  $p_k$  on model output  $Y_i$ . Matrix  $\tilde{S}$  is composed from several normalized sensitivity matrixes, calculated at the conditions of each measured data point using the fitting equation (for details see ref 32). Eigenvectors of matrix  $\tilde{S}$  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 from the other two; the 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 parameter estimation process was combined with the principal component analysis, and the results indicated that in some cases a transformation of the fitting equations was necessary, as described in the following sections. The Levenberg–Marquardt (LM) algorithm encoded by P. Holpár and E. Keszei<sup>33</sup> was used for the nonlinear least-squares fits.

**6.1. Ignition of CO on Pt Surface.** Catalytic oxidation of carbon-monoxide can be described by the following equations:



The overall reaction of CO combustion is  $\text{CO} + 0.5 \text{O}_2 \rightarrow \text{CO}_2$ ; thus,  $\sigma = 0.5$  and  $m = 1$ .

**6.1.1. Literature Data for Adsorption and Desorption Parameters.** Experiments show that increasing the fuel/oxygen ratio the ignition temperature increases, indicating that initially the surface is covered with CO. No experimental result was found on the order of adsorption and desorption of CO, but most modeling studies assume second-order adsorption ( $n_{\text{CO,A}} = 2$ )<sup>3,9,34–37</sup> and first-order desorption ( $n_{\text{CO,D}} = 1$ ).<sup>3,9,11,34,37–40</sup>

Adsorption and desorption of O<sub>2</sub> on the Pt(111) surface was investigated by Campbell et al.<sup>41</sup> using molecular beam/surface scattering techniques. Desorption was found to be of almost second order, whereas adsorption was of second order at 320 K and of first order at 520 K, closer to the heterogeneous ignition temperatures. Williams et al.<sup>42</sup> studied OH radical desorption from polycrystalline Pt foil exposed to mixtures of H<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O for surface temperatures between 1000 and 1800 K by laser-induced fluorescence. Data were analyzed using first-order adsorption and desorption, but they claimed that “using second-order adsorption/desorption did not affect the qualitative results of our model calculations”. Some modeling studies used first-order adsorption,<sup>22,38</sup> but most modeling studies assumed second order<sup>4,6,21,37,39,43–45</sup> or third order<sup>25,46</sup> adsorption. Kulginov et al.<sup>5</sup> also assumed third-order adsorption but claimed that using second-order adsorption of O<sub>2</sub> provided almost as good results. Peng and Dawson<sup>47</sup> found first-order desorption kinetics of O<sub>2</sub> from polycrystalline Pt at 700 K by temperature-programmed desorption mass spectrometry. Some modeling studies assumed second order,<sup>11,21,34,45,48,49</sup> whereas in other studies, the authors assumed first order<sup>4,38,39</sup> desorption kinetics.

The sticking coefficient of CO on Pt surface has been measured several times. Campbell et al.<sup>50</sup> determined  $S_{\text{CO,0}} = 0.84 \pm 0.05$  at 310 K on Pt(111) surface. Other authors

determined zero coverage sticking coefficients in the range of 0.6–0.8 on the Pt(111) surface<sup>51–55</sup> and  $S_{\text{CO},0} = 1$  on the polycrystalline Pt surface.<sup>56</sup> Accordingly, in all modeling studies,  $S_{\text{CO},0} = 0.84$  was used (see, e.g., refs 3, 11, 22, 34, 37, 38, and 49).

There is much larger uncertainty of the O<sub>2</sub> sticking coefficient on the polycrystalline Pt surface. Coefficients of 0.02 and 0.06,<sup>57</sup> 0.05,<sup>56</sup> 0.14,<sup>58</sup> and 0.16<sup>47</sup> have been measured. In modeling studies, a wide variety of temperature-independent sticking coefficients have been used, like 0.0003,<sup>22</sup> 0.003,<sup>38,40</sup> 0.01,<sup>39</sup> 0.02,<sup>5,25</sup> 0.023,<sup>11,14,46,59</sup> 0.0279,<sup>7</sup> 0.03,<sup>4</sup> 0.04,<sup>42,48</sup> 0.07,<sup>49</sup> 0.1,<sup>37</sup> and 0.279.<sup>21,60</sup> Deutschmann et al.<sup>3,6,34</sup> usually use a temperature-dependent sticking coefficient of  $0.07 \times (300/T)$ .

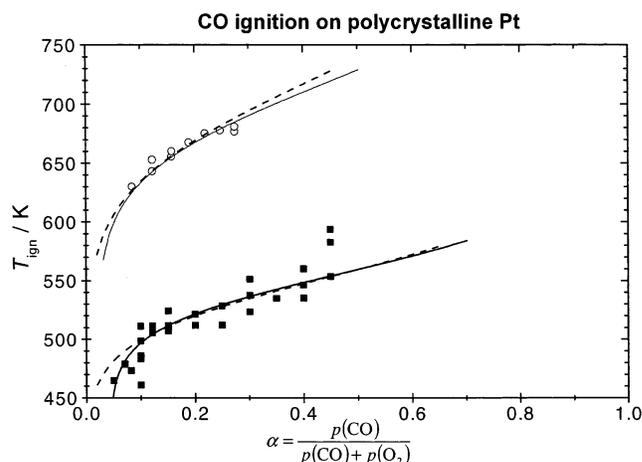
The measured CO desorption activation energies from the Pt(111) surface are 98<sup>61</sup> and 146 kJ/mol.<sup>50,54</sup> No data was found for the desorption from polycrystalline platinum. In modeling studies, 125.5,<sup>3,22,34,38</sup> 142.4,<sup>39</sup> 146,<sup>9</sup> 152.5,<sup>11,40</sup> and 184.1 kJ/mol<sup>37</sup> have been used.

The single experimentally determined desorption preexponential was  $A_{\text{CO,D}} = 1.25 \times 10^{15} \text{ s}^{-1}$  assuming first-order desorption.<sup>50</sup> In modeling studies, several values in the range of  $A_{\text{CO,D}} = 8.5 \times 10^{12}$ – $9.4 \times 10^{16} \text{ s}^{-1}$  have been used assuming first-order desorption kinetics<sup>3,9,34,37–40</sup> or  $A_{\text{D,CO}} = 10^{17} \text{ m}^2 \text{ mol}^{-1} \text{ s}^{-1}$  assuming second-order desorption kinetics.<sup>11</sup>

**6.1.2. Determined Adsorption and Desorption Parameters.** The catalytic ignition of CO on Pt surfaces was studied by Cho and Law<sup>8</sup> and Rinnemo et al.<sup>9</sup> using wire in flow (WIF) experimental geometry and Garske et al.<sup>62</sup> using stagnation point flow geometry. The Garske data were recently reanalyzed by Aghalayam et al.<sup>37</sup> Data measured by Cho and Law were reanalyzed several times,<sup>3,13,15,34,37</sup> similarly to the data obtained by Rinnemo et al.<sup>13,15,37</sup>

Experimental CO ignition data of Cho and Law<sup>3,8,34</sup> and Rinnemo et al.<sup>9</sup> were fitted here using eqs 46 and 53. Data of Garske et al.<sup>62</sup> and some data of Rinnemo et al.<sup>9</sup> could not be used here, because in these experiments the mole fraction of CO was so low that the condition of full fuel coverage did not fulfill.

Using eq 53, 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 two sets of experimental data were fitted simultaneously. The determined value was  $b = 1.03 \pm 0.10$ , and the corresponding fitted curves are given by dashed lines in Figure 1. Also, assuming several possible integer adsorption orders, fitting was attempted based on eq 53 with the corresponding fixed  $b$  values. Systematic deviation between the experimental data and the calculated data of the best fit was found for all cases except for  $b = 1$ . Therefore, the adsorption reaction orders of CO and O<sub>2</sub> can be assumed to be equal. Assuming that  $b = 1$  and using eq 46, values of  $E_{\text{CO,D}}$ ,  $S = S_{\text{CO},0}/S_{\text{O}_2,0}$ , and  $A_{\text{CO,D}}$  were fitted. Principal component analysis of this equation gave the following result: 1st parameter group: eigenvector ( $E$ : -1.00,  $S$ : 0.00,  $A$ : 0.00), eigenvalue 12.1; 2nd parameter group: eigenvector ( $E$ : 0.00,  $S$ : -0.82,  $A$ : 0.57), eigenvalue  $3.50 \times 10^{-6}$ ; 3rd parameter group: eigenvector ( $E$ : 0.00,  $S$ : 0.57,  $A$ : 0.82), eigenvalue  $3.32 \times 10^{-9}$ . This means that using eq 46, the activation energy of desorption can be determined separately and effectively, but  $S$  and  $A$  are interdependent and are separately not very effective. The values of eigenvector components give the hint that ratio  $A/S$  could be fitted independently and effectively. Therefore, eq 46 was transformed to the following form:



**Figure 1.** Surface ignition temperature for CO ignition. The experimental data of Rinnemo et al.<sup>9</sup> and of Cho and Law<sup>8</sup> are plotted with solid squares and open circles, respectively. Dashed lines denote curves fitted to the two sets of data points simultaneously, using eq 53. Fitted value of the ratio of adsorption orders is  $b = 1.03 \pm 0.10$ . Solid lines denote fitted curves to both sets of data points using eq 60. Determined values are  $E_{\text{CO,D}} = 107.2 \pm 12.7 \text{ kJ/mol}$ ,  $S_{\text{CO},0}/S_{\text{O}_2,0} = 41.2 \pm 8.5$ , and  $A_{\text{CO,D}} = 4.0 \times 10^{13} \pm 8.1 \times 10^{13}$ .

$$\frac{\Gamma \Delta_r H L_c \left( \frac{A_{\text{F,D}}}{S} \right) E_{\text{F,D}} \exp(-E_{\text{F,D}}/RT)}{\lambda RT^2 \left( \sigma \frac{X_{\text{F}}}{X_{\text{O}}} \sqrt{\frac{W_{\text{O}}}{W_{\text{F}}} - \frac{1}{S}} \right)} = 1 \quad (60)$$

Using this equation, the fitting parameters now are  $E$ ,  $A/S$ , and  $1/S$ . Principal component analysis of eq 60 gave the following result: 1st parameter group: eigenvector ( $E$ : -1.00,  $A/S$ : 0.00,  $1/S$ : 0.00), eigenvalue 44.8; 2nd parameter group: eigenvector ( $E$ : 0.00,  $A/S$ : 0.00,  $1/S$ : -1.00), eigenvalue  $6.31 \times 10^{-2}$ ; 3rd parameter group: eigenvector ( $E$ : 0.00,  $A/S$ : 1.00,  $1/S$ : 0.00), eigenvalue  $7.33 \times 10^{-5}$ . This means that using the transformed eq 60, all parameters can be determined separately. Also,  $E$  and  $1/S$  are assumed to be fitted with a small standard deviation. Determination of  $A/S$  is also independent from the others but will have a higher standard deviation.

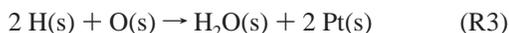
The results of parameter estimation are  $E = 107.2 \pm 12.7 \text{ kJ/mol}$ ,  $A/S = (9.74 \pm 19.57) \times 10^{11}$ , and  $1/S = 0.0243 \pm 0.0050$ . The indicated errors are 95% confidence limits. The fitted curves are shown by solid lines in Figure 1. These determined parameters were transformed to the mean values and 95% confidence limits of parameters  $E$ ,  $S$ , and  $A$ , taking into account the rules of error propagation. The determined activation energy of desorption of CO from polycrystalline Pt surface was  $E_{\text{CO,D}} = 107.2 \pm 12.7 \text{ kJ/mol}$ . The ratio of the zero coverage sticking coefficients is  $S_{\text{CO},0}/S_{\text{O}_2,0} = 41.2 \pm 8.5$ , and the preexponential factor of the CO desorption is  $A_{\text{CO,D}} = 4.0 \times 10^{13} \pm 8.1 \times 10^{13} \text{ s}^{-1}$ . If the desorption is a first-order reaction, the value of the preexponential factor does not depend on whether it is expressed with surface coverages or concentrations. If the desorption is a second-order reaction, then the preexponential factor can be expressed with surface concentrations using eq 22:  $A'_{\text{CO,D}} = 1.5 \times 10^{18} \pm 3.0 \times 10^{18} \text{ m}^2 \text{ s}^{-1} \text{ mol}^{-1}$ .

It has been demonstrated in the previous section that literature data for the adsorption and desorption of CO from the Pt surface are controversial. Modeling studies used various estimated values for parameters whose experimental values had not been available.  $E_{\text{CO,D}} = 107.2 \pm 12.7 \text{ kJ/mol}$  obtained here is the first experimentally based determination of the activation energy

of the desorption of CO from the polycrystalline Pt surface. This value is near to both the modeling values and the experimental values measured on Pt(111). The large uncertainty of the O<sub>2</sub> sticking coefficient in the literature resulted in that the ratio of sticking coefficients of CO and O<sub>2</sub> has been known only with large error. The sticking coefficient for CO on polycrystalline platinum is generally assumed to be 0.84, based on a measurement<sup>50</sup> for the Pt(111) surface. Accepting it gives  $S_{O_2,0} = 0.020 \pm 0.004$ . However, the sticking coefficient of a polycrystal is usually higher than that of the corresponding single crystal; therefore, the measured<sup>56</sup>  $S_{CO,0} = 1.00$  for the polycrystal seems realistic. Accepting it provides  $S_{O_2,0} = 0.024 \pm 0.004$ , in accordance with a measured value.<sup>57</sup> The determined  $A_{CO,D}$  value is in accordance with the value usually assumed in the literature, but its uncertainty is too high to represent new information.

Our study shows that the ratio of the kinetic order of adsorption of CO and O<sub>2</sub> is one. The adsorption of CO is usually assumed to be of second order; therefore, the adsorption order of O<sub>2</sub> may also be of second order.

**6.2. Ignition of H<sub>2</sub> on Pt Surface.** Combustion of H<sub>2</sub>/O<sub>2</sub>/diluent gas mixtures on a Pt surface proceeds via the following reactions:



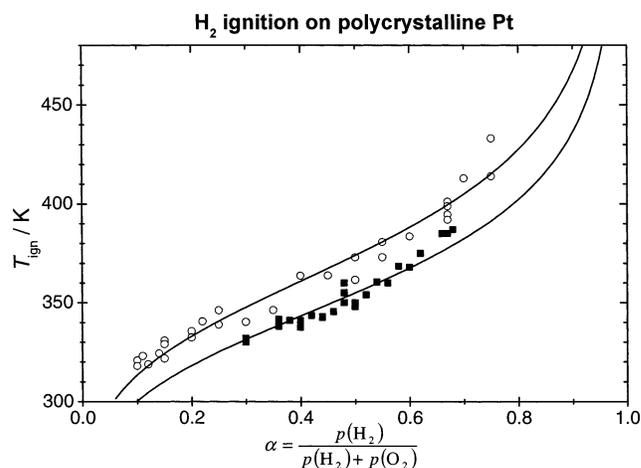
The overall reaction is  $H_2 + 0.5 O_2 \rightarrow H_2O$ ; therefore,  $\sigma = 0.5$  and  $m = 2$ .

**6.2.1. Literature Data for Adsorption and Desorption Parameters.** In some experiments first order<sup>42,63</sup> and in other experiments second order<sup>64,65</sup> kinetics was found for the adsorption of hydrogen on Pt surface. In some modeling studies,<sup>21,39</sup> second-order adsorption was assumed, but in most cases first-order adsorption<sup>3,4,6,34–36,38,43–46</sup> was considered. Kasemo et al.<sup>5,25</sup> usually assume 0.5 order adsorption kinetics. Desorption was reported to be of second order in experimental studies.<sup>65–67</sup> Experimental data in ref 42 were described by a first-order desorption model, but these data did not exclude second-order desorption. In some modeling studies second order<sup>11,21,34,48</sup> and in other studies first order<sup>4,5,25,38,39,45,49</sup> desorption kinetics was used.

The zero-coverage sticking coefficient of H<sub>2</sub> on polycrystalline Pt surface was measured to be 0.0045,<sup>65</sup> 0.04,<sup>57</sup> 0.06,<sup>68,69</sup> 0.09,<sup>70</sup> and 0.12.<sup>57</sup> Also, in some experiments, the ratio of the sticking coefficients of H<sub>2</sub> and O<sub>2</sub> was determined. The obtained values are 1.17<sup>44</sup> and 2.4<sup>57</sup> for the stagnation point flow configuration and 2.6<sup>57</sup> for the wire in the flow configuration. The values used in models include  $S_{H_2,0} = 0.046$ ,<sup>3,6,11,34,40,46,49</sup>  $S_{H_2,0} = 0.05$ ,<sup>5,14,22,25,38,39,59</sup>  $S_{H_2,0} = 0.5$ ,<sup>4</sup> and  $S_{H_2,0} = 1.0$ .<sup>7,21,48,60</sup> The ratios used in the models span a wide range from 0.65<sup>49</sup> to 166.7.<sup>22</sup> Typical values are  $S_{H_2,0}/S_{O_2,0} = 0.9$ ,<sup>3,6,34</sup>  $S_{H_2,0}/S_{O_2,0} = 2.0–2.5$ ,<sup>5,11,14,25,42,46</sup> and  $S_{H_2,0}/S_{O_2,0} = 15–17$ .<sup>4,38,40</sup>

Experimental values for the activation energy of desorption of H<sub>2</sub> from Pt surface include 67,<sup>71</sup> 73.2,<sup>66</sup> 74.0,<sup>72</sup> and 79.5 kJ/mol<sup>63</sup> for Pt(111) and 104.6 kJ/mol<sup>70</sup> for polycrystalline platinum. In most modeling studies, 67.4 kJ/mol<sup>3,11,34,36,40,49,59</sup> was used.

No experimental measurement of the preexponential coefficient of desorption was found. In modeling studies assuming



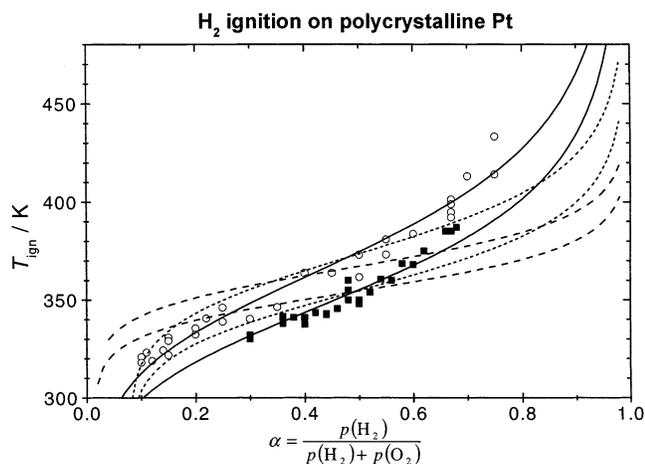
**Figure 2.** Surface ignition temperature for H<sub>2</sub> ignition. Experimental data of Deutschmann et al.<sup>74</sup> and Fassihi et al.<sup>28</sup> are plotted with solid squares and open circles, respectively. Solid lines denote fitted curves to both sets of data points using eq 53. Fitted value of the ratio of adsorption orders is  $b = 1.08 \pm 0.15$ .

second-order kinetics, values of  $5.0 \times 10^{20}$ ,<sup>40</sup>  $1.0 \times 10^{21}$ ,<sup>11,59</sup> and  $3.7 \times 10^{21}$ <sup>3,6,34,36,49</sup> were used (in mol, cm, s units); in other works, assuming first-order kinetics,  $1 \times 10^{12}$ ,<sup>4</sup>  $5 \times 10^{12}$ ,<sup>38</sup> and  $1 \times 10^{13}$ <sup>39,42</sup> was used.

**6.2.2. Determined Adsorption and Desorption Parameters.** Catalytic ignition of H<sub>2</sub> on Pt surfaces was studied by Rinnemo et al.,<sup>6</sup> Fassihi et al.,<sup>28</sup> and Cho and Law<sup>8</sup> using wire in flow experimental setup. Rinnemo et al.<sup>6</sup> carried out measurements also using a wire in stagnating gas geometry. Stagnation point flow experiments were carried out by Fernandes et al.,<sup>7</sup> Ikeda et al.,<sup>73</sup> and Deutschmann et al.<sup>74</sup> Note that the experimental data were reanalyzed several times; for example, data obtained by Fassihi et al.<sup>28</sup> were analyzed in papers 4, 5, 6, 25, 34, and data in ref 74 were studied also in ref 4.

Experimental H<sub>2</sub> ignition data from refs 28 and 74 were fitted using eqs 46, 53, and 60. Reference 28 contained data for the “wire in flow” geometry, whereas ref 74 described stagnation point flow measurements. Although the experimental conditions were very different, both data sets could be fitted simultaneously, and the experimental data could be reproduced with the same physical parameters.

Value of  $b$  was also fitted using eq 53, and value of  $b = 1.08 \pm 0.15$  was obtained. The corresponding fitted curves are given in Figure 2. Just like in the case of CO, assuming several possible integer adsorption orders, we found systematic deviation between experimental and calculated data in all cases, except for  $b = 1$ . Therefore, it was assumed that the adsorption reaction orders of H<sub>2</sub> and O<sub>2</sub> are equal ( $b = 1$ ), and then eq 46 was used. Principal component analysis of this equation gave the following result: 1st parameter group: eigenvector ( $E: -0.99$ ,  $S: -0.08$ ,  $A: 0.08$ ), eigenvalue 21.3; 2nd parameter group: eigenvector ( $E: -0.11$ ,  $S: 0.64$ ,  $A: -0.76$ ), eigenvalue  $3.45 \times 10^{-3}$ ; 3rd parameter group: eigenvector ( $E: 0.00$ ,  $S: 0.76$ ,  $A: 0.65$ ), eigenvalue  $2.80 \times 10^{-5}$ . This means that using eq 46, the activation energy of desorption can be determined separately and effectively, but  $S$  and  $A$  are interdependent. Using eq 60, the fitting parameters now are  $E$ ,  $A/S$ , and  $1/S$ . Principal component analysis now gave the following result: 1st parameter group: eigenvector ( $E: -1.00$ ,  $A/S: 0.00$ ,  $1/S: 0.00$ ), eigenvalue 6.80; 2nd parameter group: eigenvector ( $E: 0.00$ ,  $A/S: 0.30$ ,  $1/S: 0.96$ ), eigenvalue  $1.16 \times 10^{-4}$ ; 3rd parameter group: eigenvector ( $E: 0.06$ ,  $A/S: 0.953$ ,  $1/S: 0.30$ ), eigenvalue  $2.02 \times 10^{-7}$ . Thus, all new parameters can be determined



**Figure 3.** Surface ignition temperature for H<sub>2</sub> ignition. Experimental data of Deutschmann et al.<sup>74</sup> and Fassihi et al.<sup>28</sup> are plotted with solid squares and open circles, respectively. Solid lines denote fitted curves to both sets of data points using eq 60. Determined values are  $E_{\text{H}_2,\text{D}} = 43.3 \pm 5.2$  kJ/mol,  $S_{\text{H}_2,0}/S_{\text{O}_2,0} = 36.7 \pm 9.6$ , and  $A_{\text{H}_2,\text{D}} = 9.43 \times 10^{12} \pm 14.5 \times 10^{12}$ . Long and short dashed lines denote calculated curves assuming activation energy  $E_{\text{H}_2,\text{D}} = 105$  and 67 kJ/mol, respectively.

separately in this case. The results of parameter estimation are  $E = 43.3 \pm 5.2$  kJ/mol,  $A/S = (2.57 \pm 3.9) \times 10^{11}$ , and  $1/S = 0.0272 \pm 0.0071$ . The indicated errors are 95% confidence limits. The fitted curves are shown by solid lines in Figure 3. These determined parameters were transformed to the mean values and 95% confidence limits of parameters  $E$ ,  $S$ , and  $A$ . The determined value of the activation energy of the desorption of H<sub>2</sub> from Pt surface is  $E_{\text{H}_2,\text{D}} = 43.3 \pm 5.2$  kJ/mol. The ratio of the zero coverage sticking coefficients is  $S_{\text{H}_2,0}/S_{\text{O}_2,0} = 36.7 \pm 9.6$ , and the preexponential factor of the H<sub>2</sub> desorption is  $A_{\text{H}_2,\text{D}} = 9.43 \times 10^{12} \pm 14.5 \times 10^{12}$  s<sup>-1</sup>. If the desorption is a second-order reaction, the value of the preexponential factor depends on whether it is expressed with surface coverages or concentrations. The preexponential factor expressed with surface concentrations is  $A'_{\text{H}_2,\text{D}} = 3.5 \times 10^{17} \pm 5.4 \times 10^{17}$  m<sup>-2</sup> s<sup>-1</sup> mol<sup>-1</sup>.

The determined  $E_{\text{H}_2,\text{D}} = 43.3 \pm 5.2$  kJ/mol is considerably lower than the single experimental value of 104.6 kJ/mol published<sup>70</sup> in 1974. No newer results were found in the literature for polycrystalline platinum. The value of 67.4 kJ/mol used in modeling studies was published by Norton et al. in 1982, and it refers to a single crystal platinum surface; thus, it cannot be compared directly with the value obtained here. Figure 3 shows that the previously used values of 67.4 and 104.6 kJ/mol do not reproduce the ignition temperature measurements. The determined  $A_{\text{H}_2,\text{D}}$  value is in the range of the literature data, but its uncertainty is too high to represent new information. Using  $S_{\text{O}_2,0} = 0.024$  determined in the previous section,  $S_{\text{H}_2,0} = 0.88 \pm 0.40$  can be predicted. This is higher than the experimental values but close to the values used in many modeling studies. Assuming that the order of adsorption of oxygen is two results in second-order adsorption of hydrogen.

**6.3. Ignition of CH<sub>4</sub> on Pt Surface: Parameters of O<sub>2</sub> Adsorption/Desorption on Pt.** Unlike in the case of the heterogeneous ignition of CO and H<sub>2</sub>, in the case of CH<sub>4</sub>, increasing the fuel/oxygen ratio of the gas the ignition temperature decreases, because the surface is initially almost fully covered with oxygen atoms. The other difference is that the dissociative adsorption of CH<sub>4</sub> is irreversible; that is, CH<sub>4</sub> cannot desorb from the Pt surface. The overall reaction is  $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ ; therefore,  $\sigma = 2$  and  $m = 2$ .

**6.3.1. Literature Data for Adsorption and Desorption Parameters.** No experimental paper was found on the determination of the order of adsorption of CH<sub>4</sub>. In modeling studies first order,<sup>22,38</sup> second order,<sup>11</sup> and an order of 2.3<sup>35,36</sup> adsorption kinetics was assumed.

The only direct measurement<sup>75</sup> of the sticking coefficient of CH<sub>4</sub> on the Pt(111) surface gave 0.01–0.19. For this reason 0.01 was used in most modeling studies.<sup>3,35,39,59</sup> In a recent paper,<sup>76</sup> a sticking coefficient-temperature function was determined by fitting experimental data, and the sticking coefficient of CH<sub>4</sub> on the Pt surface was found to be  $6.0 \times 10^{-4}$  and almost temperature independent.

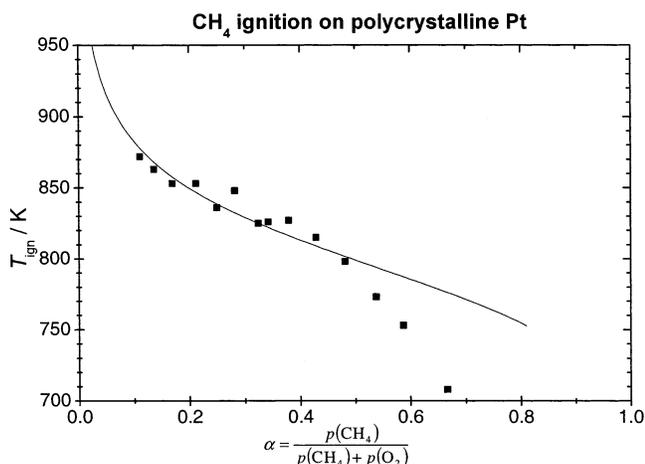
There are several measurements in good accordance on the activation energy of desorption of O<sub>2</sub> from the Pt(111) surface.  $E_{\text{O}_2,\text{D}} = 213.4$  kJ/mol was determined in papers 41 and 77 and 217.6 kJ/mol in paper 78. Repulsive energy of 133.9 kJ/mol was measured in ref 77. For polycrystalline platinum, no experimental data was found. In all modeling studies,  $E_{\text{O}_2,\text{D}} = 210$ –220 kJ/mol was used.<sup>3,4,6,11,21,22,34,36–40,42,48,49,59,60</sup> Repulsive energy was assumed to be 32,<sup>37</sup> 60,<sup>3,34,36,39,49</sup> and 133.8 kJ/mol.<sup>4</sup>

The preexponential factors used were  $A_{\text{O}_2,\text{D}} = 1.0 \times 10^{21}$ <sup>11,40,59</sup> and  $3.7 \times 10^{21}$ <sup>3,6,34,36,49</sup> assuming second-order desorption kinetics and  $5 \times 10^{12}$ <sup>38</sup> and  $1 \times 10^{13}$ <sup>4,39,42</sup> assuming first-order kinetics.

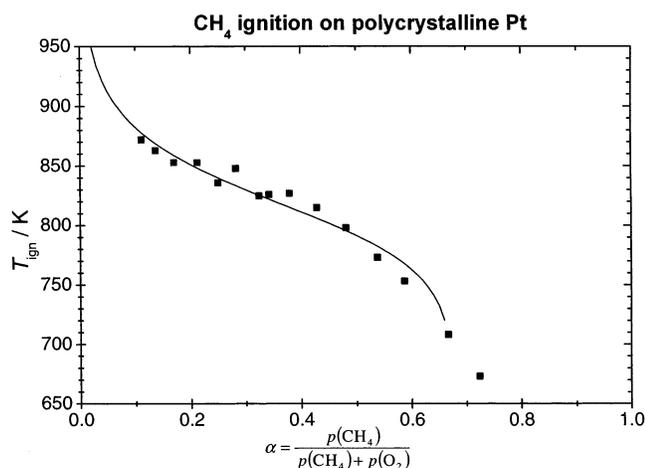
**6.3.2. Determined Adsorption and Desorption Parameters.** Griffin and Pfefferle<sup>17</sup> studied the heterogeneous ignition of CH<sub>4</sub> using a wire in flow configuration, whereas Williams et al.,<sup>16,79</sup> Behrend et al.,<sup>80</sup> and Vesper and Schmidt<sup>18</sup> used the stagnation point flow configuration. Again, the experimental data were reanalyzed in other papers. For example, the measurement described in ref 16 was investigated in papers 11, 76, and 81; the measurement of ref 80 in papers 3, 22 and 76; the measurement of ref 18 in articles 39, 76 and 82; and the measurement of ref 17 in article 76.

Experimental CH<sub>4</sub> ignition data obtained by Vesper and Schmidt<sup>18</sup> were fitted using eqs 55 and 59. Data in the other papers were not fitted, because data obtained by Williams et al.<sup>16,79</sup> were near to those measured by Vesper and Schmidt,<sup>18</sup> but the ignition temperature values could not be read accurately from the published plot, and the data obtained by Behrend et al.<sup>80</sup> refer mostly to rich mixtures where the condition of full oxygen coverage may not be satisfied.

First, eq 59 was used, where  $b$  was also a fitting parameter, and a value of  $b = 0.95 \pm 0.25$  was obtained. The fitted curve is presented in Figure 4. Assuming that the adsorption orders are integers, systematic deviation between the experimental and calculated data was not found only in the case when the adsorption orders were equal ( $b = 1$ ). Therefore, the value of  $b$  was fixed at 1.0. Principal component analysis of eq 55 gave the following results: 1st parameter group, eigenvector ( $E$ : -0.998,  $S$ : -0.057,  $A$ : 0.000) eigenvalue 31.5; 2nd parameter group, eigenvector ( $E$ : 0.054,  $S$ : -0.996,  $A$ : -0.078) eigenvalue  $1.23 \times 10^{-2}$ ; 3rd parameter group, eigenvector ( $E$ : 0.000,  $S$ : -0.076,  $A$ : 0.996) eigenvalue  $4.26 \times 10^{-5}$ . Therefore, in this case, all parameters are independent of each other, and the original eq 55 can be used.  $E_{\text{O}_2,\text{D}} = 190 \pm 34$  kJ/mol,  $A_{\text{O}_2,\text{D}} = 7.5 \times 10^{13} \pm 35 \times 10^{13}$  s<sup>-1</sup>, and  $S_{\text{O}_2,0}/S_{\text{CH}_4,0} = 5.9 \pm 0.3$  were obtained for the activation energy and the preexponential factor of the desorption of oxygen and the ratio of the zero coverage sticking coefficients, respectively. Assuming second-order kinetics for oxygen desorption, the preexponential factor expressed with surface coverages is  $A'_{\text{O}_2,\text{D}} = 2.8 \times 10^{18} \pm 13 \times 10^{18}$  m<sup>-2</sup> s<sup>-1</sup> mol<sup>-1</sup>. The plot of the fitting is shown in Figure 5.



**Figure 4.** Surface ignition temperature for CH<sub>4</sub> ignition. Dots show the experimental data of Vesper and Schmidt,<sup>18</sup> and the solid line denotes the fitted curve using eq 59. The fitted value of the ratio of adsorption orders is  $b = 0.95 \pm 0.26$ . The larger difference between the fitted curve and the last three experimental values can be attributed to the fact that the condition of full oxygen coverage is not fulfilled in the case of these rich mixtures.



**Figure 5.** Surface ignition temperature for CH<sub>4</sub> ignition. Dots show the experimental data of Vesper and Schmidt,<sup>18</sup> and the solid line denotes the fitted curve using eq 55. Fitted values are  $E_{O_2,D} = 190 \pm 34$  kJ/mol,  $S_{O_2,0}/S_{CH_4,0} = 5.9 \pm 0.3$ , and  $A_{O_2,D} = 7.5 \times 10^{13} \pm 35 \times 10^{13}$ .

The obtained  $E_{O_2,D} = 190 \pm 34$  kJ/mol is near to the previously determined experimental and estimated modeling values. Assuming  $S_{O_2,0} = 0.024$ , which was deduced from the CO ignition data,  $S_{CH_4,0} = 0.0041 \pm 0.0009$  is obtained, which is between the directly<sup>75</sup> and indirectly<sup>76</sup> determined experimental values.

## 7. Conclusions

A new method has been developed 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 is assumed that the complicated heterogeneous ignition mechanism can be basically described by four main steps: adsorption–desorption equilibrium of fuel and oxygen, the fast surface reaction of adsorbed species, and the desorption of products. 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 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 heterogeneous ignition temperature measurements and to obtain unknown physical parameters via nonlinear least-squares fitting.

The new method was used to determine the activation energy of desorption of CO, H<sub>2</sub>, and O<sub>2</sub> from the polycrystalline platinum surface. In addition, the ratios of the zero coverage sticking coefficients  $S_{CO,0}/S_{O_2,0}$ ,  $S_{H_2,0}/S_{O_2,0}$ , and  $S_{O_2,0}/S_{CH_4,0}$  and the ratios of adsorption orders were also determined. The results are summarized in Table 1. The adsorption–desorption parameters obtained were tested by calculating the predicted ignition temperature vs equivalence ratio functions and comparing them with the experimental data.

Table 1 shows that the experimentally determined values of the parameters of adsorption and desorption have been contradictory, and in many cases, only estimated values were available. The estimated values, used in modeling studies, usually span a very wide range. This work contains the first determination of desorption activation energy of CO and O<sub>2</sub> from the polycrystalline platinum surface. A new value was proposed for that data of H<sub>2</sub>, and the previously used data were shown not to reproduce the ignition temperature measurements. Confidence intervals of the parameters depend on the quality and the quantity of the available literature data. In general, ignition temperatures are very sensitive to the activation energy of desorption of the species that covers the cold catalyst and the ratio of the sticking coefficients. Only an order of magnitude estimation can be given for the preexponential factor of desorption, because the ignition temperature is not sensitive to it. When new, comprehensive and accurate, experimental data will be available, using this method, the adsorption and desorption parameters could be determined with narrower confidence intervals.

Until now, the most frequently used catalyst was the polycrystalline platinum, and the most frequently used fuels were H<sub>2</sub>, CO, and CH<sub>4</sub>. More practical applications of heterogeneous ignition systems induce the applications of new catalysts and other fuels. The method described here can be used for other fuel–oxygen mixtures and catalyst surfaces where the adsorption of one of the reactants is considerably higher than that of the other one. It can be used to determine adsorption and desorption parameters for other heterogeneous systems. The only constraint is the assumption of the initial full coverage of one of the reactants, which is satisfied in most cases, though it may fail at extreme low partial pressures of the dominant surface species or if the partial pressures of the reactants are very low (in the latter case the ratio of vacant sites is not negligible). The conditions of full coverage are discussed in the Appendix.

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**TABLE 1: Summary of the Comparison of Adsorption and Desorption Parameters Obtained Here with the Experimentally Determined and the Previously Estimated Ones (References are Available in the Text)**

	value determined here for polycrystalline Pt	experimental value for polycrystalline Pt	experimental value for Pt(111)	estimated values for polycrystalline Pt used in models
$E_{\text{CO,D}}$	107.2±12.7 kJ/mol	N/A	98 kJ/mol 146 kJ/mol	125.5–184.1 kJ/mol
$S_{\text{CO},0}$		1.00	0.6–0.84	0.84
$S_{\text{O}_2,0}$		0.02–0.16	N/A	0.003–0.279
$S_{\text{CO},0}/S_{\text{O}_2,0}$	41.2±8.5 <sup>c</sup>	6.25–50 <sup>d</sup>	N/A	3–280
CO, O <sub>2</sub> adsorption orders	$n_{\text{CO,A}}/n_{\text{O}_2,A} = 1$	$n_{\text{CO,A}} = \text{N/A}$ $n_{\text{O}_2,A} = 1 \text{ or } 2$	$n_{\text{CO,A}} = \text{N/A}$ $n_{\text{O}_2,A} = 1 \text{ or } 2$	$n_{\text{CO,A}} = 2$ $n_{\text{O}_2,A} = 2 \text{ (or 1 or 3)}$
$E_{\text{H}_2,D}$	43.3±5.2 kJ/mol	104.6 kJ/mol	67–79.5 kJ/mol	67.4 kJ/mol
$S_{\text{H}_2,0}$		0.0045–0.12	N/A	0.046–1.0
$S_{\text{O}_2,0}$		0.02–0.16	N/A	0.003–0.279
$S_{\text{H}_2,0}/S_{\text{O}_2,0}$	36.7±9.6 <sup>d</sup>	0.028–6.0 <sup>e</sup> 1.17–2.6 <sup>b</sup>	N/A	0.65–166.7
H <sub>2</sub> , O <sub>2</sub> adsorption orders	$n_{\text{H}_2,A}/n_{\text{O}_2,A} = 1$	$n_{\text{H}_2,A} = 1 \text{ or } 2$ $n_{\text{O}_2,A} = 1 \text{ or } 2$	$n_{\text{H}_2,A} = \text{N/A}$ $n_{\text{O}_2,A} = 1 \text{ or } 2$	$n_{\text{H}_2,A} = 0.5 \text{ or } 1 \text{ or } 2$ $n_{\text{O}_2,A} = 2 \text{ (or 1 or 3)}$
$E_{\text{O}_2,D}$	190±34 kJ/mol	N/A	213.4 kJ/mol 217.6 kJ/mol	210–220 kJ/mol
$S_{\text{CH}_4,0}$		N/A	0.01–0.19	0.0006–0.01
$S_{\text{O}_2,0}$		0.02–0.16	N/A	0.003–0.279
$S_{\text{O}_2,0}/S_{\text{CH}_4,0}$	5.9±0.3 <sup>e</sup>	N/A	N/A	0.3–465
CH <sub>4</sub> , O <sub>2</sub> adsorption orders	$n_{\text{CH}_4,A}/n_{\text{O}_2,A} = 1$	$n_{\text{CH}_4,A} = \text{N/A}$ $n_{\text{O}_2,A} = 1 \text{ or } 2$	$n_{\text{CH}_4,A} = \text{N/A}$ $n_{\text{O}_2,A} = 1 \text{ or } 2$	$n_{\text{CH}_4,A} = 1 \text{ or } 2 \text{ or } 2.3$ $n_{\text{O}_2,A} = 2 \text{ (or 1 or 3)}$

<sup>a</sup> Ratio of independently measured sticking coefficients. <sup>b</sup> Ratio of the sticking coefficients was measured directly. <sup>c</sup> Gives  $S_{\text{O}_2,0} = 0.024 \pm 0.004$  assuming that  $S_{\text{CO},0} = 1$ . <sup>d</sup> Gives  $S_{\text{H}_2,0} = 0.88 \pm 0.40$  assuming that  $S_{\text{O}_2,0} = 0.024$ . <sup>e</sup> Gives  $S_{\text{CH}_4,0} = 0.0041 \pm 0.0009$  assuming that  $S_{\text{O}_2,0} = 0.024$ .

## Appendix

**Conditions for the Full Coverage of the Catalyst with Fuel or Oxygen.** At low temperature, desorption of fuel and oxygen can be neglected and eqs 8 and 9 can be rewritten to

$$\frac{d\theta_{\text{F}}}{dt} = mr_{\text{F,A}} - \frac{\omega_{\text{F}}}{\Gamma} \quad (\text{A1})$$

$$\frac{d\theta_{\text{O}}}{dt} = 2r_{\text{O,A}} - \frac{\omega_{\text{O}}}{\Gamma} \quad (\text{A2})$$

The rate of the overall reaction  $\omega$  is related to the consumption rates of fuel  $\omega_{\text{F}}$  and oxygen  $\omega_{\text{O}}$ :

$$\omega = \frac{\omega_{\text{F}}}{m} = \frac{\omega_{\text{O}}}{2\sigma} \quad (\text{A3})$$

Replacing consumption rates by the rate of overall reaction  $\omega$  in eqs A1 and A2 and combining these two equations gives

$$\frac{1}{m} \frac{d\theta_{\text{F}}}{dt} - r_{\text{F,A}} = \frac{1}{2\sigma} \frac{d\theta_{\text{O}}}{dt} - \frac{1}{\sigma} r_{\text{O,A}} \quad (\text{A4})$$

$$\frac{d\theta_{\text{F}}}{dt} - \frac{m}{2\sigma} \frac{d\theta_{\text{O}}}{dt} = mr_{\text{F,A}} - \frac{m}{\sigma} r_{\text{O,A}} \quad (\text{A5})$$

Denote  $N$  the right-hand side of eq A5

$$N = mr_{\text{F,A}} - \frac{m}{\sigma} r_{\text{O,A}} \quad (\text{A6})$$

Substitute eq 17 into A6

$$N = mk_{\text{F,A}}\theta_{\text{v}}^{n_{\text{F,A}}} - \frac{m}{\sigma} k_{\text{O,A}}\theta_{\text{v}}^{n_{\text{O,A}}} \quad (\text{A7})$$

As it will be shown in the following sections, the sign of  $N$  determines the dominant surface species. The larger the absolute value of  $N$  is, the faster the homogeneous surface coverage is reached.

**Case of  $N > 0$ .** If  $N$  is positive, then from eq A5

$$\frac{d\theta_{\text{F}}}{dt} > \frac{m}{2\sigma} \frac{d\theta_{\text{O}}}{dt} \quad (\text{A8})$$

Assume that all products desorb immediately. In this case,  $\theta_{\text{p}} \approx 0$ , and  $\theta_{\text{F}} + \theta_{\text{O}} + \theta_{\text{v}} \approx 1$ . It is known from several experimental studies that, below the ignition temperature, the surface of the catalyst is almost completely covered with the reactants; thus, the ratio of the vacant sites is low:  $\theta_{\text{v}} \approx 0$ . Therefore,  $\theta_{\text{F}} + \theta_{\text{O}} \approx 1$ , and  $d\theta_{\text{F}}/dt = -d\theta_{\text{O}}/dt$ , which means that  $d\theta_{\text{F}}/dt > 0 > d\theta_{\text{O}}/dt$ . The result is the full fuel coverage:  $\theta_{\text{F}} \rightarrow 1$  and  $\theta_{\text{O}} \rightarrow 0$ .

Examine eq A7 to obtain the condition of the full fuel coverage

$$N = mk_{\text{F,A}}\theta_{\text{v}}^{n_{\text{F,A}}} - \frac{m}{\sigma} k_{\text{O,A}}\theta_{\text{v}}^{n_{\text{O,A}}} > 0 \quad (\text{A9})$$

Divide both sides with  $mk_{\text{O,A}}\theta_{\text{v}}^{n_{\text{O,A}}}$  and reformulate the inequality

$$\frac{k_{\text{F,A}}}{k_{\text{O,A}}} > \theta_{\text{v}}^{n_{\text{O,A}} - n_{\text{F,A}}} \quad (\text{A10})$$

Three different cases can be distinguished:  $n_{\text{O,A}} - n_{\text{F,A}} = 0$ ;  $n_{\text{O,A}} - n_{\text{F,A}} > 0$ ; and  $n_{\text{O,A}} - n_{\text{F,A}} < 0$ .

$n_{\text{O,A}} = n_{\text{F,A}}$ . In this case, the right-hand side of eq A10 is 1. Therefore, using eq 17

$$\frac{k_{\text{F,A}}}{k_{\text{O,A}}} = \sigma \frac{S_{\text{F},0} X_{\text{F}}}{S_{\text{O},0} X_{\text{O}}} \sqrt{\frac{W_{\text{O}}}{W_{\text{F}}}} > 1 \quad (\text{A11})$$

This inequality shows that fractions on the left-hand side should be large enough. The ratio of the molar masses  $W_i$  is on the order of 1 for CH<sub>4</sub> and CO and on the order of 10 for H<sub>2</sub>. For stoichiometric mixtures,  $\sigma X_F/X_O = 1$ ; thus,  $S_{F,0}$  has to be larger than  $S_{O,0}$  if the adsorption orders are equal.

$n_{O,A} > n_{F,A}$ . Because  $\theta_v \ll 1$ , raising it to a large enough positive power results a number near zero. Thus, if  $n_{O,A} \gg n_{F,A}$ , then there is no further condition of the full fuel coverage (unless there is an extremely lean mixture). If  $n_{O,A} - n_{F,A}$  is close to zero, then this case becomes similar to the previous one, and the additional condition of  $S_{F,0} > S_{O,0}$  has to be also valid at the usual equivalence ratios.

$n_{O,A} < n_{F,A}$ .  $\theta_v \ll 1$ , and raising it to a negative power results in a large number on the right-hand side of the inequality. In this case, the full fuel coverage requires an extremely rich mixture or very large difference in the sticking coefficients.

**Case of  $N < 0$ .** If  $N$  is negative, then from eq A5

$$\frac{d\theta_F}{dt} < \frac{m}{2\sigma} \frac{d\theta_O}{dt} \quad (\text{A12})$$

Assume again that all products desorb immediately. Employing similar arguments as above, the result is the full oxygen coverage of the surface:  $\theta_O \rightarrow 1$  and  $\theta_F \rightarrow 0$ .

Examine eq A7 to obtain the condition of the full fuel coverage

$$N = mk_{F,A} \theta_v^{n_{F,A}} - \frac{m}{\sigma} k_{O,A} \theta_v^{n_{O,A}} < 0 \quad (\text{A13})$$

Divide both sides with  $mk_{F,A} \theta_v^{n_{F,A}}$  and reformulate the inequality

$$\frac{k_{O,A}}{\sigma k_{F,A}} > \theta_v^{n_{F,A} - n_{O,A}} \quad (\text{A14})$$

Again, three different cases can be distinguished:  $n_{F,A} - n_{O,A} = 0$ ;  $n_{F,A} - n_{O,A} > 0$ ; and  $n_{F,A} - n_{O,A} < 0$ .

$n_{F,A} = n_{O,A}$ . In this case, the right-hand side of eq A14 is 1. Therefore, using eq 17 This inequality shows that fractions on

$$\frac{k_{O,A}}{\sigma k_{F,A}} = \frac{1}{\sigma} \frac{S_{O,0}}{S_{F,0}} \frac{X_O}{X_F} \sqrt{\frac{W_F}{W_O}} > 1 \quad (\text{A15})$$

the left-hand side should be large enough. The ratio of the molar masses  $W_i$  is on the order of 1 for CH<sub>4</sub> and CO and on the order of 0.1 for H<sub>2</sub>. For stoichiometric mixtures,  $\sigma X_F/X_O = 1$ ; thus,  $S_{O,0}$  has to be larger than  $S_{F,0}$  if the adsorption orders are equal.

$n_{F,A} > n_{O,A}$ . Because  $\theta_v \ll 1$ , raising it to a large enough positive power results in a number near zero. Thus, if  $n_{F,A} \gg n_{O,A}$ , then there is no further condition of the full oxygen coverage (unless there is an extremely rich mixture). If  $n_{F,A} - n_{O,A}$  is close to zero, then this case becomes similar to the previous one, and the additional condition of  $S_{O,0} > S_{F,0}$  has to be also valid at the usual equivalence ratios.

$n_{F,A} < n_{O,A}$ .  $\theta_v \ll 1$ , and raising it to a negative power results in a large number on the right-hand side of the inequality. In this case, the full oxygen coverage requires extremely lean mixture or very large difference in the sticking coefficients.

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