

# Isothermal catalytic combustion of *n*-pentane/air mixtures on platinum wire

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**Abstract** The transient response of the input power necessary to maintain isothermal conditions after a step temperature perturbation applied to a platinum wire immersed in a gaseous fuel/air mixture allows for the measurement of the reaction heat flow rate, directly related to the rate of the catalytic combustion. The S-shaped variation of this rate in time is employed to evaluate the induction period of the catalytic ignition. The effect of mixture composition, total pressure, and catalyst temperature on the induction period for the catalytic ignition of lean to stoichiometric *n*-pentane/air mixtures on isothermally heated platinum wire is reported and discussed. The mixture composition was varied between 1.40 and 2.56% *n*-pentane in air, the total pressure between 20 and 101 kPa, and the wire temperature between 470 and 600 K. The reaction rates, turnover frequencies, overall and partial reaction orders, and activation energies were determined from the analysis of the obtained results and compared to other reported data.

**Keywords** Catalytic combustion · Reaction heat flow rate · *n*-Pentane/air mixtures · Induction period

## Introduction

The catalytic combustion of alkanes, a field of increasing interest related to a cleaner conversion of chemical energy

into other forms of usable energy, has been the subject of many basic and applied investigations. Notable results have been reported for commercial applications [1, 2] in parallel with a gradual understanding of the detailed mechanism associated with the chemical reaction and with the heat and mass transfer, responsible for the kinetics of the overall process [3–5]. A well-known difficulty for such kinetic studies arises mostly from the strong exothermic effect of reaction, leading to significant temperature changes of the catalyst. In many experimental configurations, especially for supported metal catalysts, the relatively slow heat removal from the catalyst surface results in its overheating with respect to the support material [6]. The effect can be mitigated by working with very high fuel dilutions or/and with a high recirculation rate and can partly explain the differences in the kinetic parameters reported by different authors. Recent studies have been devoted to the measurement of the spatial temperature distribution in operando conditions and confirmed the existence of significant differences between the catalyst temperature and that of its solid and gas environment [6]. At the same time, a novel approach on the kinetics of catalytic combustion has been recently reported. It is based on the in situ, spatially resolved Raman measurements of major species and temperature over the reactor boundary layer in a laminar channel-flow reactor, accompanied by planar laser-induced fluorescence measurements of the OH radical. In this way both the temperature and gas phase composition necessary for kinetic analysis can be simultaneously monitored. The new technique has been applied to investigate the kinetics of methane combustion over platinum in the pressure range 4–16 bar [7], to identify the impact of large exhaust gas dilution on both heterogeneous and homogeneous combustion of fuel-lean CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> mixtures on platinum [8], and also to investigate the heterogeneous and the coupled

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hetero-/homogeneous combustion of fuel-lean propane/air mixtures over platinum [9]. At this level of resolution, the experimental data have been compared favorably with the numerical predictions using detailed kinetic models [10, 11]. On the other hand, the possibility to prevent the catalyst overheating and to maintain accurate isothermal conditions during a kinetic investigation would allow a better separation of the contributions brought about by different operational variables. A simple technique, able to fulfill these requirements, but with a narrower range of applications, was already described in several previous articles [12–14]. It is a microcalorimetric method [3, 15] and consists in heating a thin platinum wire, immersed in a fuel/air mixture, according to a quasi-step temperature profile and measuring the variation of the input power necessary to maintain a constant temperature. When an exothermal catalytic reaction occurs on the wire surface, the necessary input power decreases proportionally with the surface reaction rate. The measurement of the associated reaction heat flow rate and of the related surface reaction rate in isothermal conditions can be accomplished during both transient ignition and subsequent steady state combustion. As long as no other additional heat producing or consuming processes occur around the wire, the temperature gradient remains constant even during the transient period, a behavior different from other experimental configurations. For a relatively narrow range of variables the reaction rate exhibits a typical S-shape variation in time during the transient regime which allows for the measurement of the associated induction period. The results obtained for the ignition of lean to stoichiometric *n*-pentane/air mixtures using this technique are reported and discussed. Although *n*-pentane is present in many systems of practical importance, only few kinetic studies referring to its catalytic combustion [16] have been published as compared to C<sub>1</sub>–C<sub>4</sub> alkanes.

## Experimental method

The experimental setup and procedure have been described in details in several previous articles [12–14], and only a brief description is given here. A platinum wire (from Aldrich) of 0.1 mm diameter and 4.5 cm length is mounted in the center of a cylindrical test cell of 9 cm diameter and height. Its resistance  $R_w$  represents an arm of a Wheatstone bridge and it is connected in series with a standard resistor  $R_{std} = 5 \Omega$ . The bridge is fed from a dc stabilized power supply through a specially designed circuit which maintains a constant resistance  $R_w$  and consequently a constant wire temperature  $T_w$ . This temperature can be calculated if  $R_w$  and  $R_w^0$  (resistance at 0 °C) are known, according to available calibration procedures. To obtain a quasi-rectangular

temperature profile of the wire, a previously charged capacitor at an appropriate voltage is discharged at the beginning of the process with a rise time of approximately 2 ms. This voltage is selected by trial and error until the quasi-rectangular temperature profile is obtained. The isothermal variation of the input power on the wire induced by an exothermic reaction occurring on the platinum surface can be conveniently monitored by measuring the voltage drop  $U_{std}$  across the standard resistor. In order to obtain a property related to the reaction heat flow rate, the heat transferred to the surrounding gas through convection, conduction, and radiation as well as the heat transferred to the feeding and measuring conductors must be taken into account and eliminated. Since the fuel/air mixtures are sufficiently diluted, their heat transfer properties are very close to those of the air at the same pressure and wire temperature. Consequently the reaction heat flow rate  $dQ_r/dt$  on the platinum wire can be calculated as the difference between the input power in air and in fuel/air mixture:

$$dQ_r/dt = (R_w/R_{std}^2) \cdot [(U_{std}^2)_{air} - (U_{std}^2)_{mixture}] \quad (1)$$

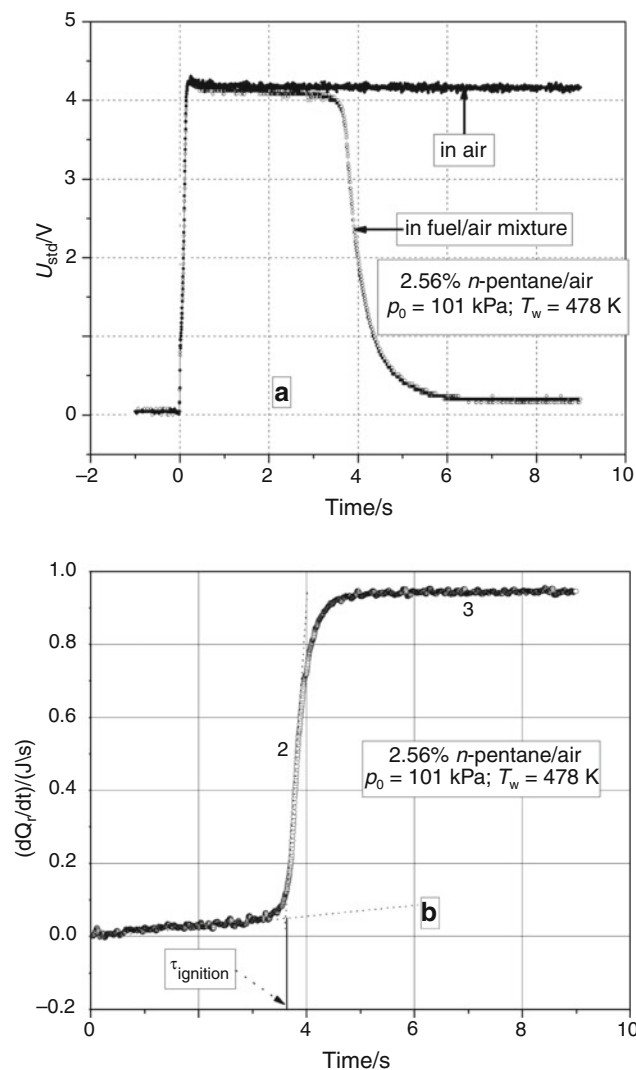
It is related to the catalytic reaction rate  $r_R$  through:

$$r_R = \frac{1}{\Delta^c H_T^0 \cdot S} \cdot \frac{dQ_r}{dt} \quad (2)$$

where  $\Delta^c H_T^0$  is the standard heat of combustion at temperature  $T$  and  $S$  the wire surface. For lean to stoichiometric mixtures  $\Delta^c H_T^0$  is assumed to have the same value, characteristic for total combustion to CO<sub>2</sub> and H<sub>2</sub>O. Typical experimental  $U_{std}$  and calculated  $dQ_r/dt$  versus time diagrams are given in Fig. 1. It can be seen that during the induction period, when the catalytic reaction is kinetically controlled,  $dQ_r/dt$  has lower values and increases slowly; then, after the induction period, it increases quickly approaching the mass transfer limit.

The lower value of  $U_{std}$  after approximately 6 s in Fig. 1a is a limitation of the input power regulation circuit which cannot work for voltages lower than approximately 0.2 V. In this way, if the reaction heat flow rate is larger, the feeding voltage cannot be decreased under this limit and the wire temperature can be higher than the calculated one. Consequently only those measurements with  $U_{std} > 0.2$  V can be used to calculate the limiting reaction heat flow rates, characteristic for diffusion control.

With  $\Delta^c H_T^0 \approx \Delta^c H_{298}^0 = 3271.73$  kJ/mol and  $S = 1.41 \times 10^{-5}$  m<sup>2</sup>, the diagram given in Fig. 1b can be converted into an  $r_R$  versus time diagram. Moreover, when an accepted figure for atomic surface density of platinum-exposed atoms is used, the corresponding turnover frequency can be evaluated. The *n*-pentane/air mixtures of known concentrations were obtained using the partial pressures method and were kept in stainless steel cylinders



**Fig. 1** a Experimental  $U_{std}$  versus time diagram; b calculated  $dQ_r/dt$  versus time diagram for a stoichiometric *n*-pentane/air mixture

24 h after preparation. Liquid *n*-pentane was injected into a previously evacuated flask and let to vaporize. The vapors were mixed with air at total pressures of 4–5 bar. To obtain reproducible results it was necessary to heat (activate) the platinum wire in air at  $p_0 = 101$  kPa and at temperatures higher than 800 K for at least 5 min before each experiment. The result is an apparent combustion on the entire wire length. Otherwise, the ignition and the subsequent combustion can occur only on a restricted segment of the platinum wire. When the wire temperature is decreased, a limiting ignition temperature can be measured. Under this value the ignition, as a sudden decrease of  $U_{std}$ , is not visible although the exothermic combustion reaction is still detectable. At higher temperatures the induction periods become undetectably small, being of the same order of magnitude with the rise time of the quasi-rectangular temperature jump. Gas pressure and platinum wire

temperature measurements were performed as described before. All calculations are based on the assumption that the wire temperature is uniform (without transversal or longitudinal gradients). From the recorded diagrams the ignition temperatures,  $T_{ign}$ , induction periods,  $\tau_i$ , catalytic reaction heat flow rates,  $dQ_r/dt$ , catalytic reaction rates,  $r_R$ , and turnover frequencies, TOF were calculated. For the leanest mixture (1.40% *n*-pentane) the extinction temperatures at various pressures were also measured. The error limits throughout the article are given for a 95% confidence level.

**Results and discussion**

**Ignition temperatures**

The ignition temperatures  $T_{ign}$  at  $p_0 = 101$  kPa as a function of *n*-pentane concentration and of the stoichiometric mixture (2.56%) as a function of total pressure are given in Tables 1 and 2, respectively, as the averages between the highest non-ignition and lowest ignition temperatures (with a resolution of  $\sim 2$  K).

The data given in Table 1 indicate a decrease of the ignition temperature with increasing fuel concentration, similar with that reported for other alkanes [3, 4, 17, 18]. For excess oxygen the combustion reaction can be approximated as a first-order process with respect to fuel [17] and the following relationship has been used to evaluate the overall activation energy  $E_a$  [17]:

$$C_F / (T_{ign} - T_0)^2 = \alpha_1 \cdot e^{E_a/RT_{ign}} \tag{3a}$$

This relationship has been extended for an arbitrary reaction order,  $n$ , occurring during a kinetically controlled regime [18]:

$$C_F^n / T_{ign}^2 = \alpha_2 \cdot e^{E_a/RT_{ign}} \tag{3b}$$

where  $C_F$  is the molar fuel concentration at gas temperature  $T_0$  or a quantity proportional to it,  $\alpha_1$  and  $\alpha_2$  are constants,  $E_a$  is the activation energy, and  $R$  is the ideal molar gas

**Table 1** Ignition temperatures for investigated mixtures at  $p_0 = 101$  kPa

$C\%$ ( <i>n</i> -pentane)	1.40	1.70	2.00	2.30	2.56
$T_{ign}/K$	493.0	486.5	488.0	484.5	476.0

**Table 2** Ignition temperatures for the stoichiometric (2.56% *n*-pentane) mixture at various initial pressures

$p_0/kPa$	101	80	60	40	20
$T_{ign}/K$	476	477	478	479	481

constant. The parameters  $E_a$  and  $n$  can be evaluated from two sets of experiments changing either the flow rate at constant composition, or the fuel concentration at constant flow rate [18].

Since our method is primarily based on the ignition temperature measurements in stagnant mixtures at various total pressures, the relationship (3b) was used taking into account both the fuel and oxygen partial reaction orders  $n_F$  and  $n_{Ox}$ , because fuel and oxygen concentrations are of the same order of magnitude.

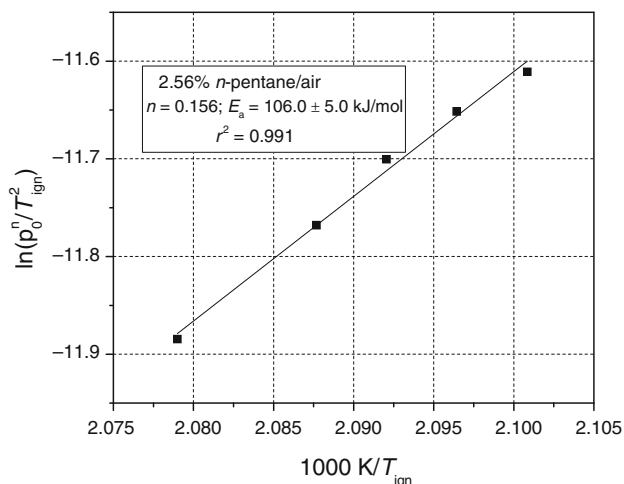
For a certain composition the relationship (3b) takes the form [14]:

$$p_0^n / T_{\text{ign}}^2 = \alpha_3 \cdot e^{E_a/RT_{\text{ign}}} \quad (4)$$

where  $\alpha_3$  is a constant and  $n$  is the overall reaction order  $n = n_F + n_{Ox}$ .

The regression analysis of data given in Table 2, using the relationship (4), gives  $E_a = 106.0 \pm 5.0$  kJ/mol. The result is illustrated in Fig. 2. The average overall reaction order,  $n = 0.156$ , was evaluated from the pressure dependence of the induction period, which will be discussed further.

Even if the ignition temperature has a small variation within the range of experimental data for this system and the relationship (3b) was derived for non-isothermal conditions, the correlation seems to be satisfactory and the result agrees well with that obtained from the analysis of the induction period. However, the results of similar processing of data measured for lower fuel concentrations, having higher errors, are quite erratic and do not exhibit a significant trend. The relatively large dispersion of experimental data accompanying small changes of the ignition temperature with the total pressure is likely to result,



**Fig. 2** Evaluation of the overall activation energy from the ignition temperature variation with the total pressure

especially during transient measurements, from the notable sensitivity of the catalytic reactivity to small changes of the platinum surface, frequently referred to in the literature [19].

The data given in Table 1 can also be analyzed using a model proposed by Vesper and Schmidt [4] for lower alkanes. According to this model, the modified equivalence ratio  $\Theta$ , defined as  $\Theta = \phi/(1 - \phi)$ , where  $\phi$  is the equivalence ratio, is given by:

$$\Theta = \left[ 1 - \frac{\kappa}{T_{\text{ign}}^2} \exp(-E_a/RT_{\text{ign}}) \right]^{-1} \quad (5)$$

where  $\kappa$  is a constant. Based on the data given in Table 1, the nonlinear regression of Eq. 5 gives  $E_a = 75 \pm 20$  kJ/mol a result following the trend reported for lower alkanes [4], but with large uncertainties and significantly lower than the above figure (106 kJ/mol). Similar differences in the kinetic parameters have been also found for other alkanes when using different methods, and these can be attributed to both experimental and model characteristic features (see the references below).

### Induction periods

The induction period (or ignition delay)  $\tau_i$ , measured between  $\approx 150$  ms and several seconds, depends on mixture composition, its total pressure  $p_0$ , and wire temperature  $T_w$ . A simple relationship giving the analytical form of this dependence in gas phase has been obtained assuming that  $\tau_i$  is proportional to the inverse of the overall reaction rate [20]. The ignition delay  $\tau_{i,g}$  for a homogeneous gas phase auto-ignition is then given by:

$$\begin{aligned} \tau_{i,g} \propto 1/r_{R,g} &= \beta_1 \cdot C_{F,g}^{-n_{F,g}} \cdot C_{Ox,g}^{-n_{Ox,g}} \cdot e^{E_a/RT_g} \\ &= \beta_2 \cdot p_0^{-ng} e^{E_a/RT_g} \end{aligned} \quad (6)$$

where  $r_{R,g}$  (in  $\text{mol m}^{-3} \text{s}^{-1}$ ) is the gas phase reaction rate,  $\beta_1$  and  $\beta_2$  are proportionality constants, and  $ng = n_{F,g} + n_{Ox,g}$  is the overall reaction order. Similar forms of this relationship are currently used to describe the pressure, temperature, and composition dependence of the ignition delay [21, 22]. The induction delay represents also a valuable tool used to describe the decomposition of solids [23].

For a catalytic surface reaction, a similar Arrhenius-type relationship can be used for the reaction rate [24] and the related ignition delay:

$$\tau_{i,s} \propto 1/r_{R,s} = \sigma_1 \cdot C_{F,s}^{-n_{F,s}} \cdot C_{Ox,s}^{-n_{Ox,s}} \cdot e^{E_a/RT_s} \quad (7)$$

where  $r_{R,s}$  is the surface reaction rate (in  $\text{mol m}^{-2} \text{s}^{-1}$ ) and  $\sigma_1$  is a proportionality constant. The surface concentrations of fuel  $C_{F,s}$  and oxygen  $C_{Ox,s}$  can be related with the

corresponding gas phase concentrations,  $C_{F,g}$ ,  $C_{Ox,s}$ , through Freundlich-type equations of the form:

$$C_{F,s} = a_F \cdot C_{F,g}^{b_F} \text{ and } C_{Ox,s} = a_{Ox} \cdot C_{Ox,g}^{b_{Ox}} \tag{8}$$

where  $a_F$ ,  $a_{Ox}$ ,  $b_F$ ,  $b_{Ox}$  are temperature-dependent parameters. Substituting (8) in (7), grouping all the proportionality constants in  $A_1$ , and assuming that the temperature dependence of the reaction rate is essentially given by the exponential factor, one obtains:

$$\begin{aligned} \tau_{i,s} &= A_1 \cdot C_{F,g}^{-(n_F \cdot b_F)} \cdot C_{Ox,g}^{-(n_{Ox} \cdot b_{Ox})} \cdot e^{E_a/RT_s} \\ &= A_1 \cdot C_{F,g}^{-m_F} \cdot C_{Ox,g}^{-m_{Ox}} \cdot e^{E_a/RT_s} \end{aligned} \tag{9}$$

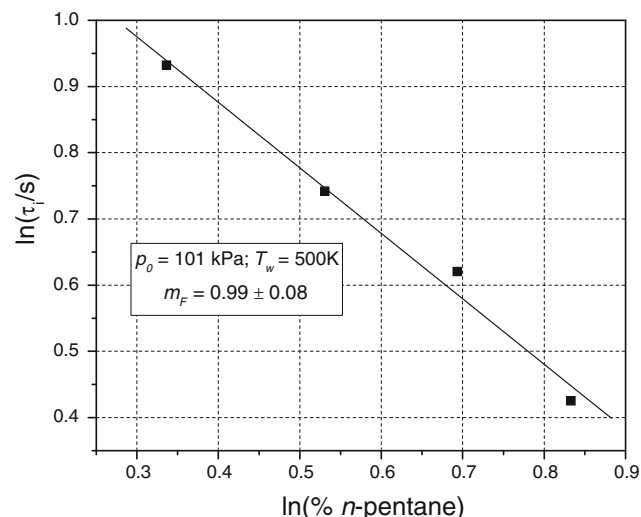
or,

$$\tau_{i,s} = A_2 \cdot p_0^{-n} \cdot e^{E_a/RT_s} \tag{10}$$

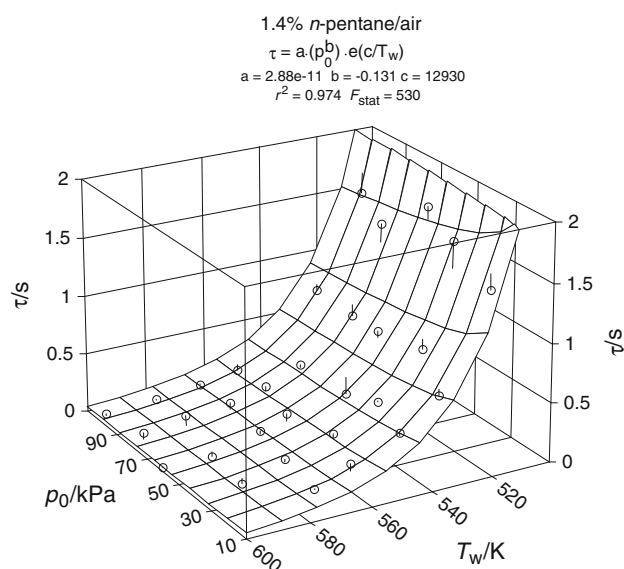
$m_F + m_{Ox} = n$  are the partial and overall reaction orders with respect to gas phase concentrations and total pressure, respectively. The constants  $\sigma_1$ ,  $a_F$ , and  $a_{Ox}$  ensure the dimensional homogeneity of Eq. 9 relating a surface property,  $\tau_{i,s}$ , with the gas phase composition,  $C_{j,g}$ . From the definition relationship  $r_{R,s} = \Delta C_s^*/\Delta t \approx \Delta C_s^*/\tau_i$  it can be seen that the constants  $A_1$  and  $A_2$  include also a critical amount  $\Delta C_s^*$  of a component required to initiate the ignition, taken as the increase of the surface concentration of an active intermediate due to temperature increase, to active intermediate multiplication, or to both processes [9].

The partial reaction order with respect to fuel  $m_F$  was evaluated at  $p_0 = 101$  kPa and  $T_w = 500$  K as shown in Fig. 3. The obtained value, close to unity, is in good agreement with the results reported for other alkanes in similar or different conditions [13, 25].

Since the pressure dependence of the induction period at constant temperature is experimentally more difficult to



**Fig. 3** Evaluation of the partial reaction order with respect to *n*-pentane



**Fig. 4** A 3D regression analysis of the induction period dependence on pressure and temperature

obtain, the overall reaction order was evaluated using a 3D nonlinear regression analysis of data  $\tau_i$  as a function of both  $p_0$  and  $T_w$ . A typical result is illustrated in Fig. 4 for the 1.40% *n*-pentane/air mixture.

The overall reaction order for this system,  $n = 0.13$ , together with  $m_F = 1$ , implies  $m_{Ox} \approx -0.87$ , indicating a low sensitivity of the induction period with respect to the total pressure and a more pronounced inhibiting effect of oxygen. Similar results were found for other fuel concentrations without a significant trend within the explored concentration range.

The results are given in Table 3 and indicate that the overall reaction order (the pressure exponent of the reaction rate) is a small positive number,  $0 < n < 1$  (the average for all fuel concentrations is  $n = 0.156$ ), in agreement with the reported data for combustion of other alkanes on platinum, indicating that the overall reaction rate increases with the increasing pressure [7, 9, 12–14, 26–28].

When compared to other reported data, the pressure exponent of the catalytic reaction rate, with an average value  $n = 0.156$ , is within the range of expected values ( $0 < n < 1$ ), but smaller than those reported for lower alkanes: 0.47 (between 1 and 16 bar) for methane [7], 0.25–0.39 (between 0.1 and 1 bar) for ethane [26], 0.75 (between 1 and 7 bar) [9] or 0.30 (between 0.2 and 0.7 bar) for propane [27], 0.20–0.36 (between 0.1 and 1 bar) for *n*-butane [13]. All these figures have been obtained measuring the catalytic reaction rate or the ignition delay at different total pressures. The overall reaction order can also be calculated as the sum of the partial reaction orders with respect to fuel and oxygen, maintaining a constant total pressure (1 bar) by adding an inert gas. The results are 0.4,

**Table 3** Fitting parameters resulted from the 3D regression analysis of  $\tau_i$  dependence on  $p_0$  and  $T_w$ 

C%	np	$a/s$	$-b$	$(E_a = c \cdot R)/\text{kJ mol}^{-1}$	$r^2$	$F_{\text{statistic}}$
1.40	31	$(2.9 \pm 3.3) \times 10^{-11}$	$0.131 \pm 0.039$	$107.5 \pm 5.1$	0.974	530
1.70	36	$(2.4 \pm 4.0) \times 10^{-12}$	$0.196 \pm 0.080$	$119.0 \pm 7.3$	0.962	412
2.00	28	$(1.0 \pm 1.8) \times 10^{-11}$	$0.100 \pm 0.062$	$109.5 \pm 7.6$	0.939	191
2.30	26	$(2.7 \pm 4.5) \times 10^{-10}$	$0.145 \pm 0.057$	$96.6 \pm 6.6$	0.944	192
2.56	25	$(2.8 \pm 4.7) \times 10^{-12}$	$0.210 \pm 0.048$	$113.2 \pm 6.4$	0.965	302

$\tau_i = a \cdot (p_0/\text{kPa})^b \cdot e^{c/T_w}$ , with  $\tau_i$  in seconds and  $T_w$  in K; np is the number of experimental points

0.5, 0.2, and 0.4 for  $C_1 - n-C_4$  alkanes [28], respectively, or close to 1.0 [27]. From these few data, measured in quite different conditions (pressure, temperature, composition), it is difficult to establish the dominant factors within the simple model of the overall single-step model. Nevertheless, it can be easily verified that the Langmuir adsorption isotherm, commonly used to describe the kinetics of a catalytic reaction, can be also fitted by a Freundlich isotherm with the concentration exponent ( $b_F$  or  $b_{ox}$  in Eq. 7) closer to unity or to zero for weaker or stronger adsorption, respectively. It is thus expected that the pressure exponent of the catalytic reaction rate will be lower for higher alkanes like  $n$ -pentane, which adsorb more strongly on the platinum surface. However, this possible trend can be altered by the superposition of other thermodynamic and kinetic factors like temperature, pressure, rate of adsorption, etc.

The activation energies calculated from the parameter  $c$  are similar with the results obtained in isobaric conditions (at 101 kPa). Similar values were also reported for  $n$ -butane/air mixtures [14]. The lack of any significant trend of activation energies with respect to fuel concentration, within the limits of experimental errors, results from Table 4.

The reported values are in good agreement with the figure obtained from the ignition temperature analysis presented above (106.0 kJ/mol). The measurement of the ignition temperatures has been recently used for the analysis of the thermokinetic oscillations during the heterogeneous catalytic oxidation of ethanol [29].

**Table 4** Activation energies (in kJ/mol) from variation of induction period with catalyst temperature: evaluated from a 2D regression analysis  $\tau_i = F_1(T_w)$  at  $p_0 = 101$  kPa and from a 3D regression analysis  $\tau_i = F_2(p_0, T_w)$ 

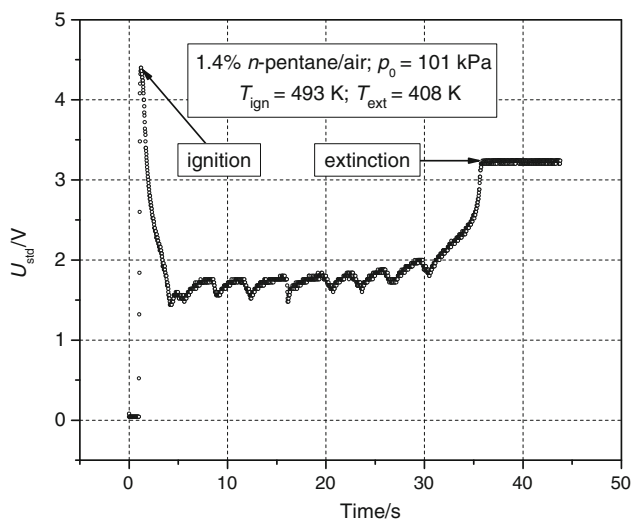
% $n$ -Pentane	$E_a$ from 2D regression	$E_a$ from 3D regression
1.40	$102 \pm 10$	$108 \pm 5$
1.70	$96 \pm 6$	$119 \pm 7$
2.00	$95 \pm 5$	$110 \pm 8$
2.30	$94 \pm 7$	$97 \pm 7$
2.56	$98 \pm 9$	$113 \pm 6$

### Reaction rates and turnover frequencies

The described experimental method enables to calculate the reaction heat flow rate  $dQ_r/dt$  and the catalytic reaction rate  $r_R$ , according to Eqs. 1 and 2. For the stoichiometric mixture (2.56%  $n$ -pentane) at  $p_0 = 101$  kPa and  $T_w = 478$  K,  $dQ_r/dt$  increases from zero to approximately 0.0565 J/mol characteristic for the end of the induction period (see Fig. 1b) and the catalytic reaction rate from zero to approximately  $1 \times 10^{-3}$  mol  $m^{-2} s^{-1}$ . The last figure can be compared with the collision frequency of fuel molecules  $v_F^* = p_F/(2\pi M_F RT_w)^{1/2} = 61.1$  mol  $m^{-2} s^{-1}$ . The ratio  $r_R/v_{HC}^* \leq 1.64 \times 10^{-5}$  suggests a kinetically controlled process. The corresponding turnover frequency given by  $TOF = r_R/\Gamma_{Pt}$  with  $\Gamma_{Pt} = 2.49 \times 10^{-5}$  mol  $m^{-2}$  [25] for atomic surface density of polycrystalline platinum exposed atoms is approximately 40.2  $s^{-1}$ . This figure is of the same order of magnitude with the data reported by other researchers for the combustion of other alkanes on platinum [25, 28]. It can be slightly overestimated due to the increased platinum surface, as compared to the geometrical value, during its activation which results in its roughening [12].

### Ignition, autothermal combustion, extinction

Ignition and extinction phenomena are intrinsic steps of the catalytic combustion playing an important role in the safe operation of various combustion devices. For lower alkanes it has been found that the catalytic ignition induced by an external heat source can be followed by autothermal combustion, when the process continues without any external heat input. Specifically, for an electrically heated platinum wire or foil, the combustion continues even after the input power has been cut off [4]. All investigated  $n$ -pentane/air mixtures exhibited autothermal behavior, except for the lowest concentration (1.40%), where the step decrease of the input power resulted in extinction at lower temperatures than those of ignition. The time evolution of  $U_{std}$  at  $p_0 = 101$  kPa is given in Fig. 5. The procedure was described in details in a previous paper [14]. The results are given in Table 5.



**Fig. 5**  $U_{\text{std}}$  versus time diagram illustrating the extinction of catalytic combustion. The peaks pointing downwards represent the step decrease of the input power; ignition is marked by a sudden decrease of  $U_{\text{std}}$  (and therefore of the input power), while extinction is marked by a sudden increase

**Table 5** Ignition and extinction temperatures of 1.40% *n*-pentane/air mixture on platinum wire

$p_0/\text{kPa}$	101	80	60	40	20
$T_{\text{ign}}/\text{K}$	493	494	502	504	508
$T_{\text{ext}}/\text{K}$	408	412	416	421	423

The results obtained in these conditions, with extinction temperatures lower than the ignition ones, similar with those reported for other systems and experimental configurations [30], are different from those reported for other alkanes using a stagnation-point flow configuration when the bifurcation diagram indicates higher extinction temperatures, as compared with the corresponding ignition temperatures, owing to reaction heat generated by combustion [4]. They contribute to a better understanding of the thermal runaway hazards encountered in catalytic combustion as well as in condensed media [31].

## Conclusions

From the transient response of the input power necessary to maintain isothermal conditions after a step temperature perturbation applied to a platinum wire immersed in a fuel/air mixture, the catalytic ignition temperatures, induction periods, catalytic reaction rates, and associated turnover frequencies for lean to stoichiometric *n*-pentane/air mixtures were measured. The measurements were performed for mixtures containing 1.40, 1.70, 2.00, 2.30, and 2.56% *n*-pentane at 20, 40, 60, 80, and 101 kPa. The wire

temperature range (470–600 K) was selected between the ignition temperature and the temperature for which the induction period was significantly larger than the rise time of the step temperature perturbation. The analysis of the ignition temperature variation according to fuel content and total pressure, by using already accepted models, resulted in activation energy of the ignition process on platinum in agreement with other alkane/air mixtures. The isothermal ignition diagrams allow also the measurement of the induction period and its dependence on gas composition, total pressure, and catalyst temperature. The analysis of the recorded data on the basis of a simple equation allowed the evaluation of the fuel reaction order ( $n_{\text{F}} = 1$ ), overall reaction order ( $n \approx 0.156$ ), and overall activation energy ( $E_{\text{a}} = 94\text{--}119$  kJ/mol) referring to catalytic ignition of *n*-pentane/air mixtures on platinum. The evaluation of the reaction rate and of the corresponding turnover frequency at the end of the induction period of combustion indicated that the process is kinetically controlled. For the mixtures containing *n*-pentane between 1.70 and 2.56% the catalytic combustion was autothermal. For the leanest investigated mixture (1.40% *n*-pentane in air) the decrease of the input power and, therefore, of the catalyst temperature allowed the measurement of the extinction temperatures, lower than the ignition temperatures.

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