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OVERALL KINETICS FOR THE CATALYTIC IGNITION OF ETHANE-AIR MIXTURES ON PLATINUM

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ABSTRACT. The overall kinetics of the catalytic ignition of a stoichiometric ethane/air mixture on an isothermally heated platinum wire is studied. The isothermal regime, achieved in an original experimental set-up, allows the direct measurement of the reaction rate in various operational conditions and the determination of the overall activation energy and reaction order on the basis of a previously reported kinetic model. The results are discussed and compared with other data obtained using different experimental techniques and models.

Keywords: *catalytic combustion, ignition, ethane/air mixture, isothermal, kinetics*

INTRODUCTION

The catalytic combustion of alkanes represents one of the most important ways to reduce the pollutant emissions which unavoidably accompany the conversion of chemical energy stored in fuels into other forms of energy. The high temperature combustion of alkanes in air, within the specific flammable ranges, between the lower flammability limit and the stoichiometric concentration, promotes the NO_x formation with unwanted consequences on the environment. The heterogeneous catalytic combustion of the same fuels, occurring at much lower temperatures, leads to a drastic reduction of NO_x formation. Moreover, the catalytic combustion on solid catalysts allows the process to occur for fuel concentrations much lower than the lower flammability limits. The catalytic combustion has consequently a valuable potential in many applications like the radiant heaters, catalytic combustors for power production, removal of hazardous air pollutants etc. [1]. The phenomenological description of this process advanced considerably during the last decades. Less information is available for the kinetics and mechanism of the interconnected steps including mass and heat transport, fluid flow and heterogeneous chemical reactions [2]. Additionally, at higher temperatures, the simultaneous homogeneous combustion induced by

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the heterogeneous catalytic reaction plays a significant role. One of the most known difficulties associated with the kinetic studies of the combustion reactions is related to its exothermicity, which leads to catalyst heating at temperatures significantly higher than the surrounding fluid. The catalyst heating can be diminished either by working at very low reactant concentrations or at very high fluid recirculation rate. Both procedures add new difficulties for these studies. This well-known phenomenon can explain the differences reported by various researchers. For platinum wires, frequently utilized in kinetic studies [3-5], we recently described an efficient method able to maintain a constant temperature during the catalytic reaction of different fuel/air mixtures [7-10]. The results obtained for *n*-butane/air, *iso*-butane/air and propane/air mixtures demonstrated the potentialities of the proposed method. A similar analysis is presented in this paper for the stoichiometric ethane/air mixture. A quasi-step temperature perturbation of a platinum catalytic wire immersed in a fuel/air mixture is applied and the corresponding reaction heat flow rate, $dQ_r/dt = F_r$, is measured in time until the process becomes stationary. The heterogeneous catalytic reaction exhibits an induction period, τ_i, which can be measured as a function of wire temperature, T_w, total pressure, p_0 and gas composition. The analytical form of this dependence, $\tau_i = f(T_w, p_0)$, allows the determination of the overall kinetic parameters through linear regression analysis [10].

RESULTS AND DISCUSSION

The experimentally recorded reaction heat flow rate, F_r, as a function of time can be easily converted in the more relevant catalytic reaction rate, r_R, in time through:

$$r_R = (dQ_r/dt)/(\Delta^c H_T^0 \cdot S) \tag{1}$$

where $\Delta^c H_T^0$ is the standard heat of combustion at the wire temperature, and S is the surface of the platinum wire ($\Delta^c H_T^0 = \Delta^c H_{298}^0$ =1,428.61 kJ/mole and S=1.41×10^{-5} m^2). A typical result is given in Figure 1.

Two properties are available from such a plot: the length of the induction period, τ_i, and the diffusion controlled reaction heat flow rate, F_r, or the corresponding reaction rate, r_R. These properties were measured for the stoichiometric ethane-air mixture at various wire temperatures and gas pressures. Their physical significances were discussed in several previous papers. The induction period is given by [10]:

$$\tau_i = \beta \cdot (p_0/p^*)^{-n} \cdot e^{E_a/RT_w} \tag{2}$$

where β is a proportionality constant including the pre-exponential factor and a critical amount, ΔC^*, of a reactant required to initiate the ignition ($r_R = \Delta C^* / \Delta t = \Delta C^* / \tau_i$), p^* is the standard pressure (≈101 kPa), n and E_a are the overall reaction order and activation energy, respectively, and R is the universal gas constant.

On the other hand, the diffusion controlled reaction heat flow rate can be rationalized according to an Arrhenius type equation [8]:

$$dQ_r / dt = F_r = A_0 \cdot (p_0 / p^*)^n \cdot e^{-E_a / RT_w} \tag{3}$$

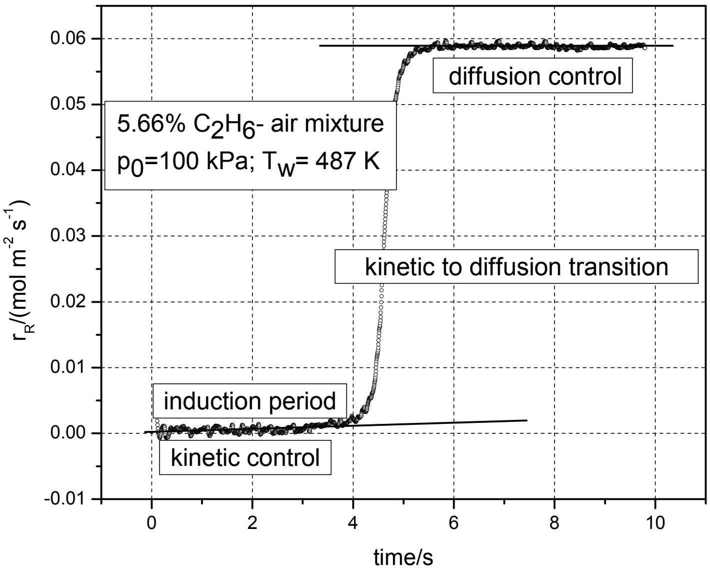

Figure 1. Variation of the surface reaction rate in time indicating the existence of an induction period and of the transition from kinetic to diffusion control

Equations (2) and (3) are used to evaluate the parameters n and E_a. It can be observed that equation (2) refers to the kinetic control, while equation (3) refers to the diffusion control.

Activation energy evaluation. A typical plot for the kinetic control is given in Figure 2 resulted from the linear regression ln(τ_i) versus $1/T_w$ of equation (2) at constant pressure. Similar plots, ln(F_r) versus $1/T_w$, were obtained also for the diffusion control from equation (3) at constant pressure.

Table 1. Kinetic and diffusion overall activation energies

p_0/kPa	E_a/(kJ/mol) ln(τ_i) *vs* 1/T_w	E_a/(kJ/mol) ln(F_r) *vs* 1/T_w
100	97.6 ± 3.2	11.5 ± 0.35
70	84.9 ± 8.5	11.54 ± 0.01
50	87.1±3.1	10.71 ± 0.37
30	74.4 ± 6.2	10.61 ± 0.36
10	75.6 ± 11.5	9.08 ± 2.43

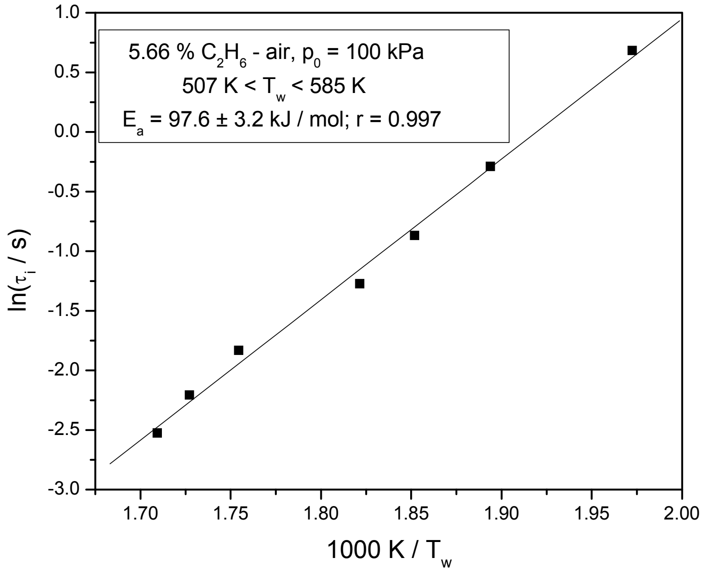

Figure 2. Evaluation of the overall activation energy for the kinetic control

The results obtained at various initial pressures for both kinetic and diffusion controls are given in Table 1. Within the limits of experimental errors no significant variation of activation energies can be detected using this method. The activation energies for the kinetic control are in good agreement with other data reported in literature: 114 kJ/mol on platinum wire from ignition temperature measurements [11], or on platinum foil in a recirculating batch reactor with mass spectrometry detection [12]; 95 kJ/mol on platinum foil in a stagnation point flow [13]; 57 kJ/mol on platinum wire from ignition temperature measurements [14]; 109 kJ/mol on platinum wires in a flow reactor [15]. When the reaction occurs on platinum dispersed on different supports the activation energy varies from 29.7 to 143 kJ/mol [16].

The activation energies for the diffusion control are within the limits accepted for these reactions.

Reaction rate and related properties evaluation. The measurement of the reaction rate for the diffusion regime offers the possibility to compare the experimental results with several relevant properties like the turnover frequency, *TOF*, the collision frequency of fuel molecules with the catalytic surface, ν_F and the ratio r_R/ν_F. The turnover frequency was calculated as $TOF = r_R/\Gamma_{Pt}$, using the literature data for the atomic surface density of platinum exposed atoms (Γ_{Pt}=2.49 × 10^{-5} mol m^{-2} [12]). The collision frequency of fuel molecules with the catalytic surface was calculated for the stoichiometric ethane-air mixture as [8]:

$$\nu_F = p_F \big/ (2\pi M_F R T_w)^{1/2} \tag{4}$$

where p_F is the partial pressure of the fuel and M_F its molar mass.

The results are given in Table 2.

Table 2. Reaction rates and associated properties for diffusion control at T_w = 549 K

p_0 kPa	r_R (mol m^{-2} s^{-1})	$10^{-3}\times TOF$ (s^{-1})	ν_F (mol m^{-2} s^{-1})	$10^4\times(r_R/\nu_F)$
100	0.0765	3.07	193	3.96
70	0.0720	2.89	135	5.33
50	0.0660	2.65	96.5	6.84
30	0.0591	2.37	57.9	10.2
10	0.0348	1.40	19.3	18.0

The *TOF* values are very large compared with other literature data [8, 10]. A possible explanation is based on the observation that the platinum wire exhibits significant catalytic activity only after heating at temperatures higher than 800 K, when the initially smooth surface becomes coarse with an increased atomic surface density. The ratio r_R/ν_F has very low values, (4-18) $\times 10^{-4}$, indicating a reduced efficiency of fuel collisions with the catalyst surface. If these values are corrected for the activation energy factor (of the order 9.6×10^{-2}), very small sticking coefficients are obtained. The data given in Table 2 indicate that the method and the measurements give realistic results for a typical heterogeneous catalytic reaction of combustion.

Reaction order evaluation. The measurements at constant temperature of the reaction heat flow rates for a diffusion controlled process and of the induction periods for a kinetically controlled process can be used to evaluate the overall reaction orders using the linear regression analysis of equations (3) and (2). The results are given in Table 3. It can be observed that the overall reaction orders have an approximately constant value of 0.34, without a significant trend. These figures are in agreement with the frequently reported order n_F=1 for alkane-air catalytic combustion and with the recognized inhibitory effect of oxygen in these reactions (n_{ox}<0), giving $n=n_F+n_{ox}<1$. The inhibitory effect of oxygen in alkane-air catalytic combustion has been attributed to its preferential adsorption on platinum surface, even at lower temperatures. The fraction of catalyst surface available for fuel adsorption is consequently very small, lowering the reaction rate for a mechanism of competitive adsorption of fuel and oxygen.

Table 3. Overall reaction orders, *n*, at different temperatures

T_w/K	ln(τ_i) *vs* ln (p_0/p^*)	ln(F_r) *vs* ln(p_0/p^*)
564	0.25 ± 0.05	0.31 ± 0.04
549	0.35 ± 0.03	0.34 ± 0.04
534	0.36 ± 0.04	0.37 ± 0.04
525	0.39 ± 0.02	0.33 ± 0.01

Critical ignition temperatures measurement and analysis. Many kinetic studies concerning the catalytic combustion of fuel-air mixtures rely upon the ignition temperature measurement for different fuel content. Starting from the assumption that the ignition is triggered when the catalyst temperature attains a critical value which ensures the transition from the kinetic control to the diffusion control, a simple relationship was proposed, allowing the evaluation of the activation energy [11]:

$$C_F\big/(T_{ign}-T_0)^2=\alpha_1\cdot e^{E_a/RT_{ign}} \tag{5}$$

where C_F is the bulk concentration of reactant and α_1 is a proportionality constant.

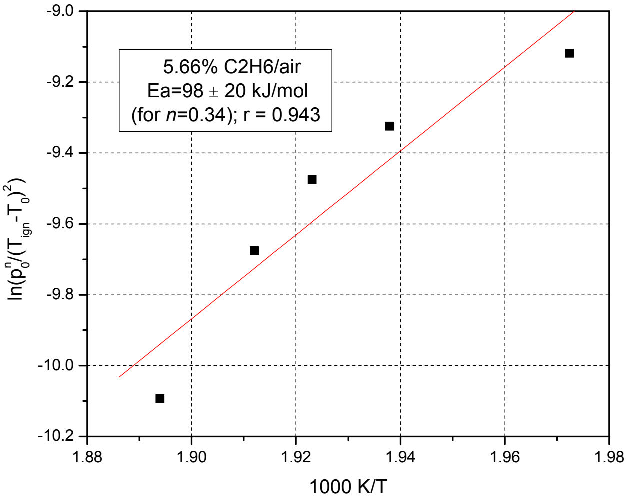

Figure 3. Evaluation of activation energy according to equation (7)

It was also assumed that the surface reaction is of first order in hydrocarbon and zero order in oxygen concentration (for large excess of oxygen). This relationship has been subsequently generalized [2] for a *n* order reaction in the form:

$$C_F^n \Big/ (T_{ign} - T_0)^2 = \alpha_1 \cdot e^{E_a / RT_{ign}} \tag{6}$$

Since our experimental technique allows the measurement of the ignition temperature at various total pressures, we recently proposed an alternative procedure for the determination of the activation energy [10] as long as $C_F^n \propto p_0^n$ for constant T_0 and fuel molar fraction:

$$p_0^n \Big/ (T_{ign} - T_0)^2 = \alpha_2 \cdot e^{E_a / RT_{ign}} \tag{7}$$

where α_2 is a proportionality constant.

A representative result is given in Figure 3. The measured activation energy is in good agreement with the results given in Table 1 for the kinetically controlled process.

CONCLUSIONS

The catalytic combustion of the stoichiometric ethane-air mixture on a platinum wire heated in isothermal conditions allows a deeper understanding of the kinetics of this heterogeneous reaction. Since the wire temperature is constant during the ignition and subsequent combustion, the self-acceleration of the reaction rate cannot be explained on the basis of the thermal ignition, which assumes a continuous increase of the catalyst temperature. From the measurement of the induction periods of the catalytic ignition at various temperatures and total pressures, the overall kinetic parameters – activation energy and reaction order – can be evaluated. The obtained results are in good agreement with those obtained using other experimental approaches. The analysis of the ignition temperature variation with the total pressure using a new model allows an alternative method for the determination of activation energy. All these results validate the proposed method and recommend it as a valuable alternative for kinetic studies concerning the heterogeneous catalytic combustion reactions.

EXPERIMENTAL SECTION

The experimental measurements were carried out using the equipment and procedure described in details previously [7-10] and given schematically in Figure 4. A platinum wire of 0.1 mm diameter and 45 mm length (99.99% from Aldrich), connected through brass conductors in a heating circuit, is immersed in the center of a cylindrical test cell of 9 cm diameter and height, containing either air or fuel/air mixture at a prescribed pressure. It is heated according to a quasi-rectangular profile, with a rise time of 1 – 2 ms using the discharge of a capacitor *C* followed by a controlled feeding system designed to maintain a constant wire temperature. A standard resistor R_{std}, connected in series with the wire of resistance R_w, forms a Wheatstone bridge with the potentiometer *P* and allows the measurement of the input power, recording the variation of the voltage drop U_{std} during the test. Any unbalance of the bridge is detected by the integrated circuit IC which readjusts the voltage applied across R_w through the series transistor *T* in order to maintain its resistance constant. The diagram U_{std} versus time contains the information necessary for the kinetic study. To evaluate the heat flow rate dQ_r/dt due to the catalytic reaction occurring on the wire it is necessary to eliminate the power dissipated through the heat transfer from the hot wire to the surroundings.

The kinetically relevant quantity dQ_r/dt can be obtained from the diagrams recorded in air and in a fuel/air mixture in similar conditions as:

$$dQ_r/dt = (R_w/R_{std}^2)\left[(U_{std}^2)_{air} - (U_{std}^2)_{mixture}\right] \tag{8}$$

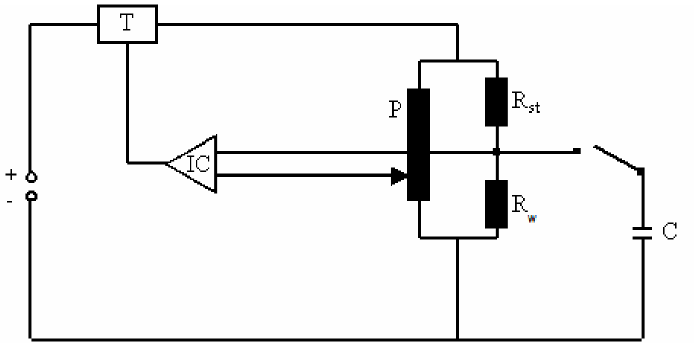

Figure 4. Schematic representation of the electrical circuit able to heat the platinum wire according to a quasi-rectangular profile

A typical recording of U_{std} is given in Figure 5.

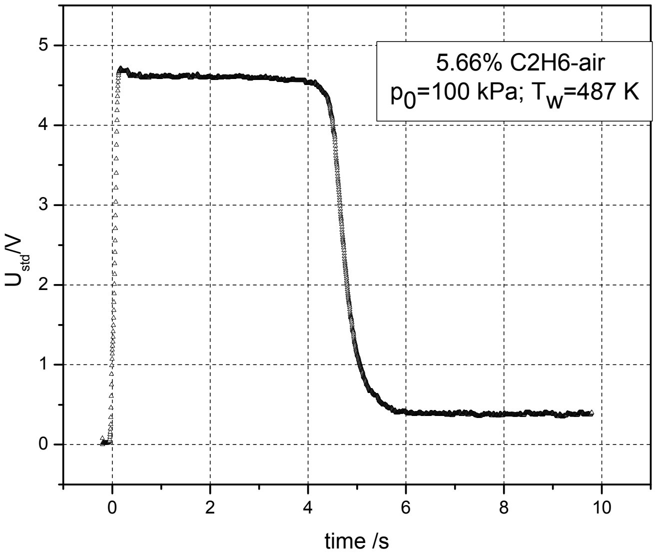

Figure 5. Recorded U_{std} versus *time* diagram

Using equation (8) and the similar diagram recorded in air (without fuel) at the same wire temperature and total pressure, a kinetic diagram given in Figure 1 can be obtained. The wire temperature is calculated according to literature recommendations as [17]:

$$T_w = 273.15 + D_0 + \sum_{i=1}^{9} D_i \cdot [\frac{x - 2.64}{1.64}]^i \tag{9}$$

where x is the ratio between the wire resistance at temperature T_w and at 273.15 K and D_0, D_j are constants given in literature [17]. All the other details were given elsewhere [7-10].

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REFERENCES

1. J. Saint-Just, J. der Kinderen, *Catalysis Today*, **1996**, *29*, 387.
2. A. Schwartz, L. Holbrook and H. Wise, *Journal of Catalysis*, **1971**, *21*, 199.
3. C. G. Rader and S. W. Weller, *American Institute of Chemical Engineering Journal*, **1974**, *20*, 515.
4. S. W. Weller and C. G. Rader, *American Institute of Chemical Engineering Journal*, **1975**, *21*, 176.
5. P. Cho and C.K. Law, *Combustion and Flame*, **1986**, *66*, 159.
6. M. A. A. Cardoso and D. Luss, *Chemical Engineering Science*, **1969**, *24*, 1699.
7. D. Oancea, D. Razus, M. Mitu and S. Constantinescu, *Revue Roumaine Chimie*, **2002**, *47*, 91.
8. D. Oancea, O. Staicu, V. Munteanu, and D. Razus, *Catalysis Letters*, **2008**, *121*, 247.
9. O. Staicu, V. Munteanu, D. Oancea, *Catalysis Letters*, **2009**, *129*, 124.
10. O. Staicu, D. Razus, V. Munteanu, D. Oancea, *Central European Journal of Chemistry*, **2009**, *7*, 478.
11. L. Hiam, H. Wise, S. Chaikin, *Journal of Catalysis*,**1968**, *9-10*, 272.
12. M. Aryafar and F. Zaera, *Catalysis Letters*, **1997**, *48*, 173.
13. G. Veser and L.D. Schmidt, *American Institute of Chemical Engineering Journal*, **1996**, *42*, 1077.
14. T. A. Griffin, L. D. Pfefferle, *American Institute of Chemical Engineering Journal*, **1990**, *36,* 861.
15. Y.-F. Yu Yao, *Industrial and Engineering Chemistry, Product Research and Development*, **1980**, *19*, 293.
16. T. F. Garetto, E. Rincon, C. R. Apesteguia, *Applied Catalysis B: Environmental*, **2007**, *73*, 65.
17. H. Preston-Thomson, *Metrologia*, **1990**, *27*, 3.