



PRESSURE EFFECT ON THE TRANSITION FROM KINETIC TO DIFFUSION CONTROL DURING CATALYTIC IGNITION

O.M. Staicu ^{*,**}, V. Munteanu ^{*} and D. Oancea ^{*}

abstract: The pressure effect on the kinetics of the catalytic ignition of stagnant stoichiometric propane/air, n-butane air and i-butane/air mixtures during the transient, early stage of ignition was investigated using a thin platinum wire heated following a quasi-rectangular profile and operated in an isothermal regime. The overall reaction order was measured and the found values (0.3 – 0.4) were discussed and explained on the basis of a simple kinetic equation.

received: October 29, 2008

accepted: November 13, 2008

Introduction

During the last time the catalytic combustion of gaseous fuel/air mixtures became a very promising procedure to convert chemical energy into heat and work with low level pollutant emissions. Noble metals proved to be very efficient catalyst and numerous laboratory studies have been performed with the aim to identify the main parameters which control the evolution of the overall process. The catalytic ignition is one of the key steps representing a sudden transition from kinetic to diffusion control [1,2]. Depending on the properties of the system, the ignition can be followed by extinction or by steady combustion. The critical conditions for ignition, extinction or stable combustion are necessary to find those constraints which ensure a safe and reliable operation of various experimental devices. Fuel nature, gas phase composition, flow regime, catalyst temperature and total pressure are the most important parameters which can be adjusted to obtain the sought result. In a previous paper we have analyzed the temperature effect on the transient period of the catalytic ignition of several alkanes/air mixtures on isothermally heated platinum wires [3]. A significant decrease of the activation energy during this period was found and explained on the basis of a simple kinetic model [4]. The present paper aims to investigate the effect of the total pressure change, from 10 to 100 kPa, on the ignition of propane and butanes/air mixtures.

* Department of Physical Chemistry, University of Bucharest, 4-12 Bd. Elisabeta, 030018 Bucharest, Roumania, *corresponding author e-mail:* doan@gw-chimie.math.unibuc.ro

** "Ilie Murgulescu" Institute of Physical Chemistry, Roumanian Academy, 202 Spl. Independentei, 060021 Bucharest, Roumania

Experimental

The description of the experimental setup and working procedure has been given elsewhere [4,5]. A thin platinum wire is connected in series with a standard resistor and, together with a potentiometer, forms a Wheatstone bridge. The bridge is fed from a stabilized power supply whose voltage is adjusted through a feedback system to maintain the bridge at equilibrium. In this state the wire temperature is maintained constant. At the beginning of the heating process, a pre-charged capacitor is discharged on the wire in order to obtain a quasi-rectangular profile of the platinum wire temperature. Measuring the resistances R_w and R_{std} and recording the voltage U_{std} , the input power on the wire can be calculated as:

$$P_{input} = (R_w / R_{std}^2) \cdot U_{std}^2 \quad (1)$$

The reaction heat flow rate, dQ_r/dt , delivered by the exothermal catalytic reaction, can be calculated as the difference between the input power in air and in a fuel/air mixture:

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

This is related with the reaction rate of the heterogeneous catalytic reaction through:

$$r_r = \frac{1}{\Delta^c H_T^0 \cdot S} \cdot \frac{dQ_r}{dt} \quad (3)$$

where $\Delta^c H_T^0$ is the standard combustion enthalpy at temperature T , which can be approximated with $\Delta^c H_{298}^0$, and S is the surface of the platinum wire.

An illustrative example of the experimental recording is presented in Fig. 1.

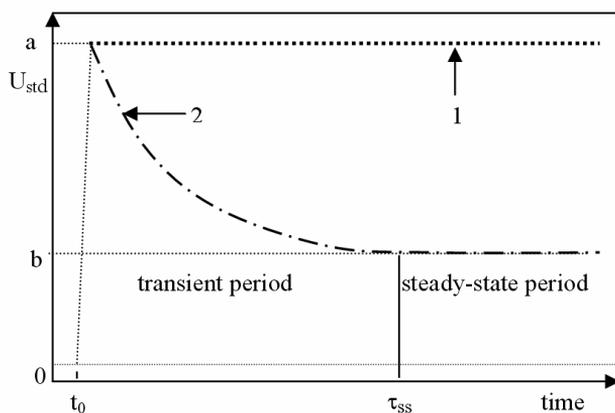


Fig. 1 Recording of U_{std} variation in time:
1) in air; 2) in a fuel/air mixture

The jump of U_{std} from a) to b) is generated by the catalytic reaction occurring on the platinum surface. The transient period is followed by steady-state combustion, installed after a characteristic time τ_{ss} . The data contained in Fig. 1 can be used to calculate the

reaction heat flow rate, dQ_r/dt during the transient period. To analyze the changes in dQ_r/dt induced by mixture composition, wire temperature or total gas pressure within the transient period, a series of measurements were carried out at various fractions of τ_{ss} , as seen in Fig. 2.

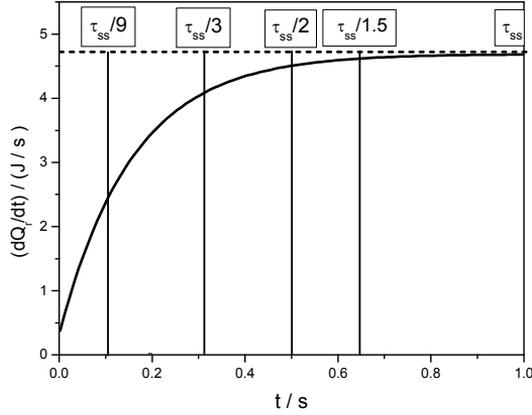


Fig. 2 Variation of the reaction heat flow rate during the transient period

Results and Discussions

It was shown that the curve in Fig. 2 can be described by a three parameter equation of the form:

$$\frac{dQ_r}{dt} = a + b \cdot (1 - \exp(-c \cdot t)) \quad (4)$$

On the other hand it was also found that the reaction rate can be conveniently rationalized using an Arrhenius type kinetic equation of the form:

$$r_R = A \cdot (p_0/p^*)^n \cdot (X_{ox}^{n_1} \cdot X_F^{n_2}) \cdot e^{-E_a/RT_w} = A_0 \cdot (p_0/p^*)^n \cdot e^{-E_a/RT_w} \quad (5)$$

where A and A_0 are preexponential factors, p_0 is the total gas pressure, p^* is the standard pressure ($p^* = 101.3$ kPa), n is the overall reaction order, X_{ox} , and X_F are the molar fractions of the oxygen and fuel, respectively, n_1 and n_2 are the corresponding partial reaction orders, E_a is the overall activation energy, R is the universal gas constant and T_w is the wire temperature.

The overall kinetic parameters E_a and n and their variations with T_w and p_0 within the transient period can be evaluated from the regressions $\text{Ln} [(dQ_r/dt)/(J/s)]$ vs $1/T_w$ and $\text{Ln} [(dQ_r/dt)/(J/s)]$ vs $\text{Ln}(p_0/\text{kPa})$ respectively. The first analysis was already analyzed and discussed [3].

Alternatively, the reaction rate can be also rationalized using a mechanistic Langmuir-Hinshelwood type kinetic equation which for low alkane adsorption takes a simpler form:

$$r_R = k_s \cdot \frac{K_F \cdot K_{ox} \cdot p_F \cdot p_{ox}}{(1 + K_F \cdot p_F + K_{ox} \cdot p_{ox})^2} \approx k_s \cdot \frac{K_F \cdot K_{ox} \cdot p_F \cdot p_{ox}}{(1 + K_{ox} \cdot p_{ox})^2} \quad (6)$$

where k_s is the rate constant of the surface reaction, K_F, K_{ox} and p_F, p_{ox} are the adsorption-desorption equilibrium constants and partial pressures of fuel and oxygen, respectively.

The results obtained for propane/air mixtures are illustrated in Fig. 3.

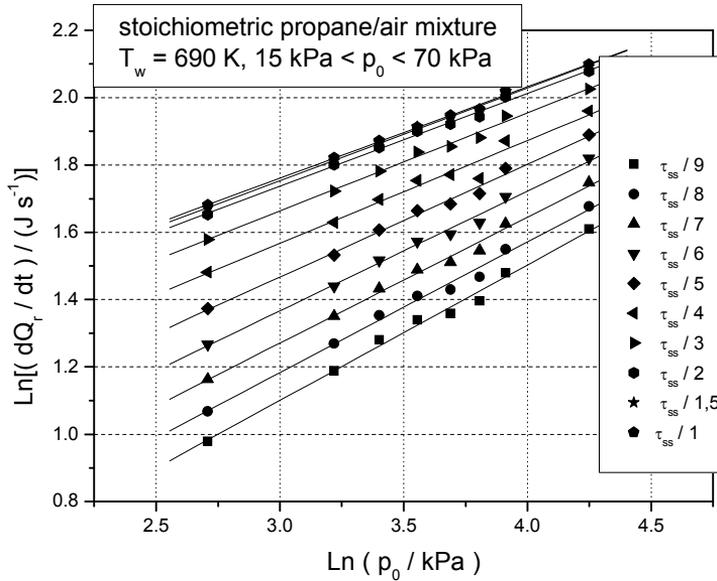


Fig. 3 Variation of the reaction heat flow rate with the total pressure

It is apparent that the relationship between $\text{Ln}(dQ_r/dt)$ and $\text{Ln}(p_0)$ is linear and has approximately the same slope from $\tau_{ss}/1$ to $\tau_{ss}/9$. For *n*-butane and *i*-butane the results were similar. Within the limits of the experimental errors the overall reaction orders varies between 0.3 and 0.4, without any apparent trend, as can be seen in Table 1. This behavior is similar with that found for steady state combustion [4], where the partial reaction order with respect to the fuel (*n*-butane) was $n_F = 1$ and with respect to oxygen was approximately $n_{ox} = -0.6$. To explain these results an improved kinetic model is presented starting from a similar one discussed before [4].

These results are in good agreement with other reported data for alkane/air catalytic combustion on noble metals which indicated that the partial reaction order with respect to fuel is approximately equal with unity while the partial reaction order with respect to oxygen is negative and less than unity, confirming its inhibiting effect due to stronger adsorption on the catalytic sites [6÷9].

Table 1 Overall reaction orders of stoichiometric propane/air mixture at various temperatures for τ_{ss}/z where $z = 9 \dots 1$

z	T _w /K		
	690	840	927
9	0.40 ± 0.01	0.30 ± 0.01	0.40 ± 0.03
8	0.40 ± 0.01	0.30 ± 0.01	0.40 ± 0.03
7	0.40 ± 0.01	0.30 ± 0.01	0.40 ± 0.03
6	0.40 ± 0.01	0.30 ± 0.01	0.40 ± 0.03
5	0.30 ± 0.01	0.30 ± 0.009	0.40 ± 0.02
4	0.30 ± 0.01	0.30 ± 0.008	0.40 ± 0.02
3	0.30 ± 0.01	0.30 ± 0.008	0.40 ± 0.02
2	0.30 ± 0.008	0.30 ± 0.006	0.40 ± 0.02
1.5	0.30 ± 0.007	0.30 ± 0.005	0.40 ± 0.02
1	0.30 ± 0.005	0.30 ± 0.005	0.40 ± 0.008

The model assumed that the form of the kinetic equation within a thin layer around the catalytic surface is of the form [4]:

$$r_R = k_r \cdot C_{F,V}^* \quad (7)$$

where k_r is a composite reaction rate constant resulted from lumping all the surface steps and $C_{F,V}^*$ is the volume concentration of the fuel within the considered thin gaseous layer. Due to the mass transport and catalytic reaction, this is different from the bulk fuel concentration equal to $C_{F,V}^0$. This hypothesis led the following kinetic equation:

$$\frac{dQ_r}{dt} = \frac{\Delta^c H_T^0 \cdot S \cdot k_D \cdot k_r \cdot C_{F,V}^0}{k_D + k_r} \cdot \left[1 - \exp\left(\frac{-(k_D + k_r)}{\phi} \cdot t\right) \right] \quad (8)$$

where k_D is the mass transfer constant and ϕ is a characteristic thickness of unit length introduced to ensure the dimensional homogeneity of the involved equations. Equation (7) gives an accurate description of the ignition transient period and a rational explanation of the activation energy variation within the transient period. When $t > \tau_{ss}$, the second factor in the right hand side of equation (8) approaches unity and the resulted kinetic equation becomes characteristic for the steady state combustion. However, taking into consideration the relationship between the molar concentration of the fuel and total mixture pressure, $C_{F,V}^0 = x_F \cdot p_0 / R \cdot T_0$, one can conclude that dQ_r/dt increases linearly with p_0 for a constant mixture composition, in disagreement with our experimental results. This should be valid only for very lean mixtures having the oxygen in large excess, when its partial reaction order is apparently zero. For mixtures with higher fuel concentrations, up to the stoichiometric ones, the kinetic equation (7) should be modified accordingly. To account for oxygen implication in the kinetic equation, the following form is proposed:

$$r_R = k_r \cdot C_{F,V}^* \cdot \varphi(C_{O_x}) = k^* \cdot C_{F,V}^*, \text{ with } k^* = k_r \cdot \varphi(C_{O_x}) \quad (9)$$

Besides the previous treatment when it was supposed that $\varphi(C_{\text{ox}})=1$, the present approach will take into account either a power law equation when $\varphi(C_{\text{ox}})=C_{\text{ox}}^m$ or a Langmuir-Hinshelwood type law when $\varphi(C_{\text{ox}})=C_{\text{ox}}/(1+K_{\text{ox}} \cdot C_{\text{ox}})^2$. The final kinetic equation takes the form:

$$\frac{dQ_r}{dt} = \frac{\Delta^c H_T^0 \cdot S \cdot k_D \cdot k_r^* \cdot C_{F,V}^0}{k_D + k_r^*} \cdot \left[1 - \exp\left(\left(-\left(k_D + k_r^*\right)/\phi\right) \cdot t\right) \right] \quad (10)$$

The equation (10) is valid for both transient and steady state periods and can take two limiting values [3]:

I. When $t \rightarrow \tau_s$, then $\exp\left(\left(-\left(k_D + k_r^*\right)/\phi\right) \cdot t\right) \rightarrow 0$ and consequently:

$$\frac{dQ_r}{dt} = a + \frac{\Delta^c H_T^0 \cdot S \cdot k_D \cdot k_r^* \cdot C_{F,V}^0}{k_D + k_r^*} = a + b_1 \cdot \frac{k_r^*}{k_D + k_r^*} p_0 \quad (11)$$

II. When $t \rightarrow 0$, then $\exp\left(\left(-\left(k_D + k_r^*\right)/\phi\right) \cdot t\right) \approx 1 - \left(\left(k_D + k_r^*\right)/\phi\right) \cdot t$, for $\left(\left(k_D + k_r^*\right)/\phi\right) \cdot t \ll 1$. Taking fractions of τ_{ss} as $t = \tau_{ss}/z$, where $z = 1 \dots 9$ one obtains for sufficiently large z :

$$\left(\frac{dQ_r}{dt}\right)_z = a + \frac{\Delta^c H_T^0 \cdot S \cdot k_D \cdot k_r^* \cdot C_{F,V}^0}{\phi} \cdot \frac{\tau_{ss}}{z} = a + b_2 \cdot k_r^* \cdot p_0 \quad (12)$$

where a , b_1 and b_2 are constants.

Equations (11) and (12) can be used to select the best choice for k_r^* : 1) $k_r^* = k_r$; 2) $k_r^* = k_r \cdot C_{\text{ox}}^m = k_{r,2} \cdot p_0^m$; 3) $k_r^* = k_r \cdot C_{\text{ox}}/(1+K_{\text{ox}} \cdot C_{\text{ox}})^2 = k_{r,3} \cdot p_0/(1+K_{\text{ox}}' \cdot p_0)^2$ to obtain an adequate agreement with experimental data.

The assumption 1) results in a linear relationship between dQ_r/dt and p_0 , in disagreement with experimental data. The assumption 2) gives two different relationships for the limiting cases I and II, both of them able to account for overall reaction order lower than unity. Since the experimental results indicate a constant overall reaction order for both $t \rightarrow \tau_s$ and $t \rightarrow 0$, this assumption is rejected. The assumption 3) gives results of similar forms – $dQ_r/dt = a + b \cdot p_0^2/(1 + d \cdot p_0)^2$ – able to account for fractional orders when $t \rightarrow \tau_s$ or when $t \rightarrow 0$. Consequently the pressure dependence of the reaction rate during the transient ignition period for the stoichiometric mixtures of propane/air, *n*-butane/air and *i*-butane/air can be satisfactorily explained using a simple three parameter equation derived by taking into account the reaction rate dependence on both fuel and oxygen concentrations. The most adequate form was found for a Langmuir-Hinshelwood model assuming a non-dissociative and competitive adsorption of fuel and oxygen on the catalytic centers, with a stronger adsorption of oxygen molecules.

Conclusions

The ignition of a gaseous stagnant fuel/air mixture using a thin isothermally heated platinum wire, according to a quasi-rectangular profile, is a sudden transition from kinetic to diffusion control, strongly dependent on both wire temperature and mixture pressure. The pressure dependence of the reaction rate within the transient period, preceding the steady state catalytic combustion, indicated an overall reaction order between 0.3 and 0.4 for the stoichiometric propane/air, *n*-butane/air and *i*-butane/air mixtures at different temperatures, without a significant trend from the beginning to the end of the transient period. The experimental results could be explained on the basis of a simple kinetic equation able to account for both temperature and pressure dependence of the overall reaction rate.

Acknowledgements: The authors acknowledge the financial support of CNCSIS through the Contract no.38/2007 for the Project ID_1008.

REFERENCES

1. Schwartz, A., Holbrook, L. and Wise, H. (1971) *J. Catal.* **21**, 199-207.
2. Rinnemo, M., Deutschmann, O. Behrendt, F. and Kasemo, B. (1997) *Combust. Flame* **111**, 312-26.
3. Staicu, O., Munteanu, V. and Oancea, D. (2008) *Rev. Roumaine Chim.* Submitted.
4. Oancea, D., Staicu, O., Munteanu, V. and Razus, D. (2008) *Catal. Lett.*, **121**(3-4), 247-54.
5. Oancea, D., Razus, D., Mitu, M. and Constantinescu, S. (2002) *Rev. Roumaine Chim.* **47**, 91-7.
6. Yu Yao, Y.-F. (1980) *Ind. Eng. Chem. Prod. Res. Dev.* **19**, 293-8.
7. Aryafar, M. and Zaera, F. (1997) *Catal. Lett.* **48**, 173-83.
8. Ma, L., Trimm, D.L. and Jiang, C. (1996) *Appl. Catal. A Gen.* **138**, 275-83.
9. Deshmukh, S.R. and Vlachos, D.G. (2007) *Combust. Flame* **149**, 366-83.