



INCIPIENT PHASE OF THE CATALYTIC IGNITION OF LEAN *n*-HEPTANE-AIR MIXTURE

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abstract: The incipient phase of catalytic ignition of 1.20% *n*-heptane-air over the surface of a heated platinum wire has been investigated at atmospheric pressure. The experimental setup allowed for ignition in isothermal condition, with quasi-rectangular rise of the wire temperature, and the recorded electrical signals accounted for compensation of the energy delivered by the chemical reaction over the catalytic surface. Activation energy was calculated via either induction period or slope of the incipient kinetic regime curve, denoted by very slow increase of the reaction rate – time dependency. The difference of the two quantities allowed for the evaluation of the energy contribution of the chemical reaction. The results are compared with previous findings for fuels of lower molecular mass.

key words: *n*-heptane-air; catalytic ignition; platinum wire; activation energy.

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Introduction

The ignition of fuel/air mixtures over heated catalysts like platinum, as either solid plate or wire, has been of interest among many theoretical or applied studies, which explore ideas for combustion with lower pollutants emissions, catalytic mineralization of volatile organic compounds or cleaner exhaust gases in automotive cars [1÷4].

Ignition of the fuel mixture is done by a rapid transition from kinetic to mass transfer control of the overall process together with an exponential increase of the reaction rate with time (Fig. 1). If the fuel is ignited under isothermal conditions then the autoacceleration process is supported by the multiplication of the active intermediates on the catalyst surface rather than excess heat generated by the chemical reaction [12].

The present work is a continuation of our previous studies on fuels with lower molecular mass [5÷12].

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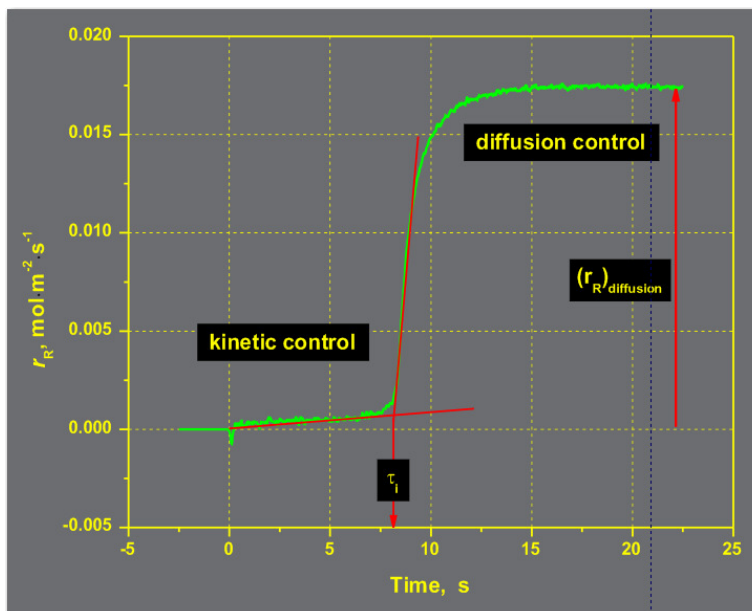


Fig. 1 Representative diagram for kinetic to diffusion transition.

Experimental

The experimental setup was previously described in detail [5,7,9]. It consists of a platinum wire (0.1 mm in diameter and 4.5 cm in length) which is assembled in a Wheatstone bridge that allows for maintaining the isothermal heating condition.

The wire is placed at the geometrical center of a cylindrical vacuum-tight explosion cell of 9 cm diameter and height. The working initial pressures were 101 and 80 kPa, respectively. Fuel mixture of 1.20% *n*-heptane in air has been prepared by partial pressures at 500 kPa absolute pressure; the mixture was allowed to diffuse for 24 h prior to experiment runs.

Results and discussion

The reaction heat flow rate, dQ_r/dt , which is recorded via computer-assisted data acquisition, is related to the catalytic reaction rate r_R through [7]:

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

where $\Delta^{\circ}H_T^0$ represents the standard heat of combustion and S_w the wire surface ($1.41 \times 10^{-5} \text{ m}^2$).

From the voltage versus time diagrams recorded for each experimental run at different initial pressure p_0 and wire temperature T_w , two parameters have been measured: the induction period, τ_i , which is the time necessary to achieve autoacceleration of the combustion over the catalyst surface (see Fig. 1), and the slope of the linear increase of the reaction rate during the kinetic control region, $\alpha = dr_R/dt$.

The results are presented in Table 1.

Table 1 *Incipient phase characteristics of n-heptane-air catalytic combustion on platinum.*

p_0 (kPa)	Wire Temperature, K	Induction period, s	Incipient slope, mol/m ²
101	572.79	0.014	2.96
101	555.02	0.032	3.52
101	542.04	0.046	1.25
101	523.82	0.054	1.10
101	512.59	0.073	0.91
101	496.29	0.105	0.77
101	480.21	0.119	0.51
101	466.76	0.136	0.47
80	572.37	0.026	4.22
80	558.11	0.039	3.07
80	543.83	0.053	1.91
80	526.70	0.074	1.78
80	512.72	0.098	1.39
80	496.93	0.117	1.02
80	481.41	0.128	0.53
80	466.28	0.140	0.47

Both τ_i and α are related to the catalytic reaction rate, and the temperature dependence of them will allow for the evaluation the overall activation energy, E_a , during the ignition process. The Arrhenius type dependencies on the temperature of the platinum are:

$$\begin{aligned}\tau_i &= a_1 \cdot \exp(E_{a,\tau} / RT_w) \\ \alpha &= a_2 \cdot \exp(-E_{a,\alpha} / RT_w)\end{aligned}\quad (2)$$

where a_1 and a_2 are proportionality constants. On the other hand, the two activation energies derived in eq. (2) have different physical significance; the induction period is related only to the adsorption of the reactants over the catalytic surface, whereas the incipient slope takes into account the supplemental energy required by the chemical activation:

$$\begin{aligned}E_{a,\alpha} &= E_{a,\text{adsorption}} + E_{a,\text{reaction}} \\ E_{a,\tau} &= E_{a,\text{adsorption}}\end{aligned}\quad (3)$$

In other words, ones can evaluate the apparent chemical activation energy by:

$$\overline{\Delta E}_a = E_{a,\alpha} - E_{a,\tau} \quad (4)$$

Figs. 2 and 3 gives the experimental data processing at atmospheric initial pressure while Figs. 4 and 5 the same for 80 kPa.

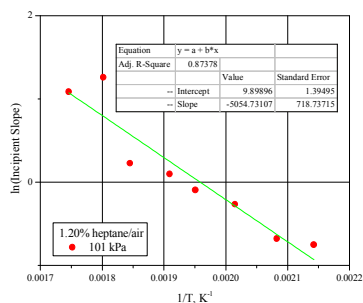


Fig. 2 Temperature dependence of the incipient slope in semilogarithmic scale; $p_0=101$ kPa

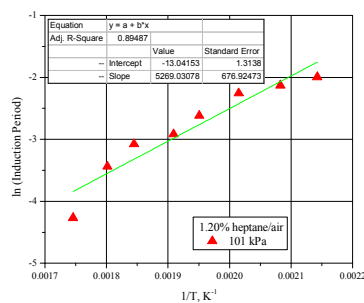


Fig. 3 Temperature dependence of the induction period in semilogarithmic scale; $p_0=101$ kPa

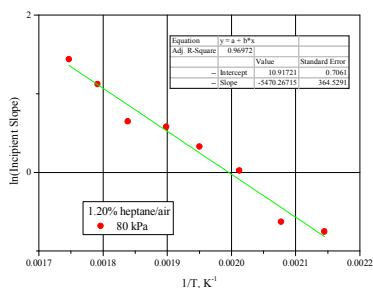


Fig. 4 Temperature dependence of the incipient slope in semilogarithmic scale; $p_0=80$ kPa

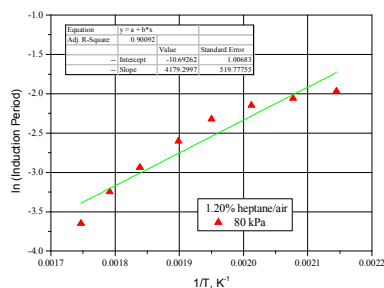


Fig. 5 Temperature dependence of the induction period in semilogarithmic scale; $p_0=80$ kPa

It has been found (see Table 2) that, within the experimental errors, the term $\overline{\Delta E}_a$ is maximum 10 kJ/mol, which tells that the energy required to activate the adsorbed species over the heated platinum surface is very small. Once the adsorption is done, the chemical reaction is very likely to occur.

Table 2 Apparent activation energies computed from Figs. 2-5.

p_0 (kPa)	E_a (kJ/mol) via Induction Period, τ	E_a (kJ/mol) via Incipient Slope, α
101	43.79 ± 5.63	42.00 ± 6.00
80	34.73 ± 4.32	45.46 ± 3.03

The value is decreased compared to our previous findings for fuels with lower molecular mass (ethane [10], propane [11], *n*-butane [5,7,8], *n*-pentane [12]).

Conclusions

The catalytic combustion of *n*-heptane/air over heated platinum has been investigated at two different initial pressures.

The energetic terms required for physical adsorption as well as for chemical activation of the fuel were evaluated from the characteristics of the incipient phase of the combustion process.

It has been found that the energy requested to activate C₇ fuels over the catalyst surface is lower than those for C₂-C₅ fuels.

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