TEMPERATURE AND PRESSURE EFFECT ON THE ISOTHERMAL CATALYTIC IGNITION OF *n*-HEXANE/AIR MIXTURES ON PLATINUM

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This paper addresses several issues associated with the isothermal catalytic ignition and combustion of lean to stoichiometric n-hexane/air mixtures on a thin platinum wire. The time evolution of the catalytic reaction rate in isothermal regime has been followed after a step temperature jump applied to the platinum wire. The ignition delays and the limiting mass transfer controlled rates of the catalytic combustion have been measured using the resulted S-shaped curves, for different fuel concentrations, wire temperatures and gas pressures. The lower and upper parts of the reaction rate *versus* time curve indicate a mechanism of acceleration associated with the surface active centers multiplication, and the mass transfer limitations, respectively. The activation energies and reaction orders for an overall single-step reaction model have been evaluated using a 3D nonlinear regression analysis under both kinetic and mass transfer control and discussed in connection with the prediction of two previously reported simplified models.

INTRODUCTION

The relatively new technique referring to the heterogeneous catalytic combustion of alkane/air mixtures has known a growing interest during the past few years both for a cleaner combustion of lower alkanes, with lower NO_x emissions, and for the removal of volatile organic compounds (VOCs) resulted from various industrial processes. Among all VOCs, hexanes are significant constituents of gasoline and are involved also in numerous processes like oil extraction, degreasing operations, textile manufacturing. The presence of *n*-hexane in different emissions and the possibility to remove it through catalytic combustion has been discussed in several recent papers.[1-8] Besides the practical aspects, the structural effects of both catalyst and fuel on the catalytic combustion mechanism proved to be of real interest. The kinetics of the catalytic combustion is of special importance in the analysis of this complex process. For simpler fuels like H_2, CO and CH_4, a detailed kinetic analysis has been possible, with major

consequences for a better understanding of the main controlling factors. For higher alkanes the detailed kinetics is still unavailable and consequently only simplified kinetics can account for the observed time evolution of the overall process, the single-step model being often the only practical solution. The kinetic models for the catalytic combustion must explain both the transient (ignition and extinction) and steady state processes, taking into account the strong exothermicity of the reaction and branching mechanism acting as positive feedbacks for the reaction rate. In order to simplify the kinetic analysis, the number of independent variables involved in this process can be reduced by using an isothermal regime. To maintain a constant temperature during a fast exothermic reaction is a difficult task which cannot be handled easily in homogeneous systems. Unlike homogeneous systems, the catalytic combustion on an electrically heated platinum wire can be performed in isothermal conditions by adjusting the input power applied to the wire in order to obtain a quasi

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rectangular temperature profile. The technique and its application for the catalytic combustion of various alkanes in air have been described in several previous papers.[9-16] The experimental procedure allows for the calculation of the variation of the reaction heat flow rate in time, which can be subsequently converted into a reaction rate *versus* time curve. The resulted S-shaped curve describes the ignition step with the associated ignition delay, followed by the transition to the steady-state combustion limited by the mass transfer from the gas to the catalyst surface.

RESULTS

The isothermal reaction rates for the catalytic combustion of lean (1.20, 1.50 and 1.80 %) and stoichiometric (2.16 %) *n*-hexane/air mixtures at 20, 40, 60, 80 and 101 kPa and temperatures between 446 and 547 K on a platinum wire of 0.1 mm diameter and 45 mm length, in stagnant gaseous mixtures, have been calculated from the primary experimental data. The calculated reaction rates, based on the measurement of the reaction heat, are attributed only to the surface catalytic reactions, neglecting the possible contribution of homogeneous reactions occurring near catalyst surface, which can be significant at higher temperatures. A typical result is given in Fig. 1.

It can be seen that the reaction rate increases continuously, even if the temperature is kept constant. This self-acceleration can be attributed to the multiplication of the surface active intermediates.

During the initial time interval, $0 - \tau_{ind}$, representing an induction period, the reaction rate is relatively low and is controlled kinetically. Afterwards, it increases exponentially being subsequently controlled by the mass transfer rate, which in stagnant mixtures is dependent on the both molecular diffusion and the natural convection induced by the temperature gradient between the platinum wire and the surrounding gas. Two useful properties can be measured directly from these curves: the induction periods, τ_{ind}, and the rates limited by the mass transfer, r_R^*, both of them being dependent on catalyst temperature and gas pressure.[14] The induction periods have been measured at the intersection of the two tangent lines, as indicated in Fig. 1. The long induction periods, measured at lower temperatures, close to the critical ignition temperatures, significantly deviate from the general trend and have been omitted from the subsequent analysis. Several selected results are given in Tables 1 and 2. For brevity not all available measurements are shown.
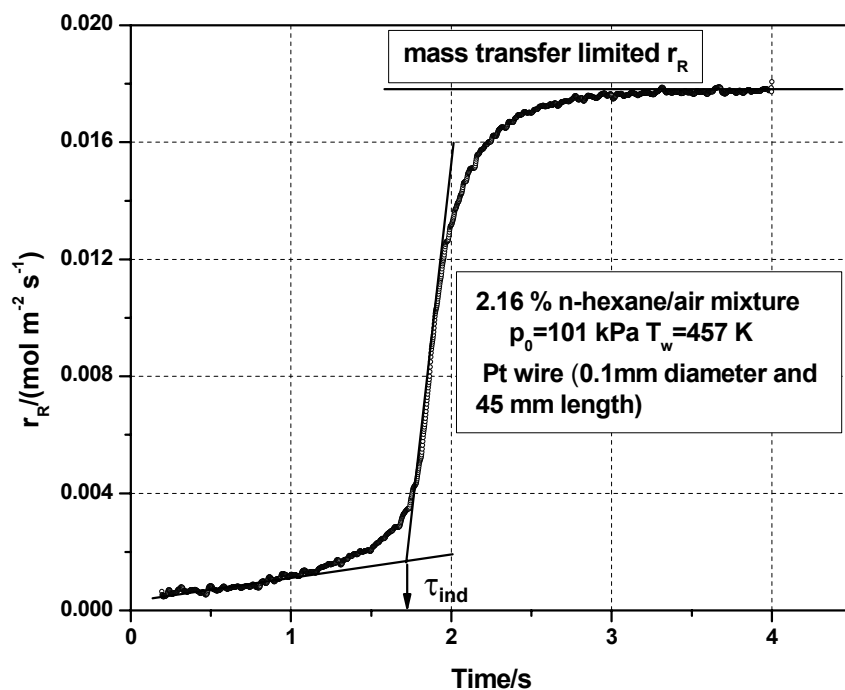

Fig. 1 – Variation in time of the catalytic reaction rate after a step temperature jump (298-457 K).

Table 1

Selected induction periods, τ_{ind} (in s), at different pressures, p_0 (in kPa), and temperatures, T_w (in K), for n-hexane/air mixtures

% Fuel	1.20		1.50		1.80		2.16	
p_0	T_w	τ_{ind}	T_w	τ_{ind}	T_w	τ_{ind}	T_w	τ_{ind}
101	517	0.08	533	0.07	502	0.20	530	0.08
101	507	0.13	518	0.10	489	0.32	515	0.10
101	492	0.21	505	0.17	475	0.75	501	0.23
101	477	0.41	493	0.28	462	1.54	485	0.39
101	465	0.79	477	0.55	450	4.22	473	0.77
80	522	0.08	540	0.07	547	0.05	518	0.12
80	506	0.15	525	0.09	533	0.09	499	0.22
80	494	0.27	509	0.18	518	0.15	485	0.49
80	480	0.49	496	0.38	506	0.25	473	0.91
80	467	0.81	483	0.64	490	0.48	456	1.94
60	521	0.09	540	0.07	528	0.07	542	0.05
60	508	0.13	524	0.10	510	0.15	527	0.08
60	496	0.28	510	0.24	496	0.27	510	0.13
60	480	0.41	495	0.42	483	0.56	498	0.28
60	467	0.78	482	0.68	470	0.97	482	0.52
40	507	0.17	538	0.08	527	0.09	530	0.07
40	495	0.24	525	0.12	511	0.16	514	0.15
40	483	0.41	512	0.21	498	0.30	500	0.25
40	468	0.76	498	0.43	485	0.54	486	0.53
40	455	1.70	482	0.72	470	1.00	472	0.96
20	–	–	542	0.08	530	0.08	528	0.08
20	–	–	527	0.14	516	0.16	517	0.18
20	–	–	512	0.28	501	0.33	502	0.29
20	–	–	499	0.42	485	0.58	487	0.58
20	–	–	484	0.75	474	0.98	474	0.99

The catalytic reaction rate is calculated according to:[10]

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

where dQ_r/dt is the experimentally measured reaction heat flow rate, $\Delta^c H_T^0 = 3886.67$ kJ/mol is the standard heat of combustion for *n*-hexane at the temperature T_w (approximated here as the standard heat of combustion at the temperature $T_0 = 298$ K), and $S = 1.41 \cdot 10^{-5}$ m^2 is the catalyst surface.

According to experimental procedure, dQ_r/dt is given by:

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

where R_w, R_{std}, are the resistances of the wire and of a standard resistor connected in series with the wire, and U_{std} is the voltage drop on the standard resistor, either in air or in the combustible mixture. All involved quantities are measured or recorded experimentally.

Table 2

Selected limiting reaction rates, r_R^* (in mol m^{-2} s^{-1}), at different pressures, p_0 (in kPa), and temperatures, T_w (in K), for n-hexane/air mixtures

% Fuel	1.20		1.50		1.80		2.16	
p_0	T_w	r_R^*	T_w	r_R^*	T_w	r_R^*	T_w	r_R^*
101	438	0.0142	550	0.0300	502	0.0240	445	0.0163
101	451	0.0154	533	0.0280	489	0.0221	445	0.0162
101	477	0.0173	505	0.0240	462	0.0176	473	0.0194
101	507	0.0213	477	0.0197	444	0.0157	501	0.0229

Table 2 (continued)

101	517	0.0232	464	0.0187	442	0.0157	515	0.0246
80	447	0.0140	552	0.0281	547	0.0272	451	0.0163
80	451	0.0146	540	0.0265	533	0.0252	456	0.0171
80	480	0.0162	509	0.0220	506	0.0217	485	0.0200
80	494	0.0181	496	0.0203	490	0.0198	499	0.0219
80	537	0.0240	453	0.0159	448	0.0152	547	0.0277
60	446	0.0130	553	0.0261	542	0.0259	452	0.0152
60	453	0.0136	540	0.0242	528	0.0240	459	0.0162
60	467	0.0146	525	0.0224	511	0.0220	470	0.0178
60	508	0.0181	482	0.0171	470	0.0176	510	0.0223
60	537	0.0227	454	0.0149	449	0.0155	542	0.0261
40	455	0.0127	554	0.0244	541	0.0238	452	0.0144
40	483	0.0143	525	0.0206	511	0.0203	472	0.0164
40	495	0.0159	512	0.0185	498	0.0189	486	0.0176
40	524	0.0190	482	0.0155	470	0.0163	514	0.0206
40	552	0.0229	453	0.0137	449	0.0144	543	0.0240
20	–	–	556	0.0210	542	0.0212	453	0.0129
20	–	–	527	0.0178	516	0.0182	474	0.0146
20	–	–	512	0.0158	501	0.0170	487	0.0156
20	–	–	469	0.0130	457	0.0132	528	0.0198
20	–	–	457	0.0121	451	0.0129	544	0.0209

Besides the two properties, the induction period and the limiting reaction rate, the shape of the reaction rate *versus* time curve offers additional information on the component steps of the ignition and steady state combustion if appropriate models are used to fit the experimental data.[10, 16] Thus the initial exponential increase suggests a branching mechanism for the surface intermediates,[16] while the final saturation trend indicates that the overall process occurs under the mass transfer control.[10] Since the detailed kinetics for this system are lacking, two previously reported simplified models are used as alternative approaches and compared with the empirical Arrhenius-type model for a single-step reaction.

DISCUSSION

The empirical single-step kinetic equations for mass transfer control and for induction period have the following forms:[10, 12, 14, 15]

$$r_R^* = \alpha_1 \cdot (p_0/p_{std})^{n_1} \cdot e^{-E_{a,*}/RT_w} \qquad (3)$$

$$\tau_{ind} = \alpha_2 \cdot (p_0/p_{std})^{-n_2} \cdot e^{E_{a,ind}/RT_w} \qquad (4)$$

where α_1 and α_2 are constants, n_1 and n_2 are the overall reaction orders, $E_{a,*}$ and $E_{a,ind}$ are the corresponding activation energies, and p_{std} is the reference pressure taken here as 1 kPa. Using data like those given in Tables 1 and 2, these parameters can be evaluated through a 3D regression analysis. An example is given in Fig. 2.

Similar results have been obtained for all investigated systems, as well as for the function $\tau_{ind} = f_2(p_0, T_w)$, which is inversely proportional to the corresponding reaction rate. The results are given in Table 3.

The overall reaction orders for both mass transfer control ($r_R^* = f_1(p_0, T_w)$) and kinetic control ($\tau_{ind} = f_2(p_0, T_w)$) vary non-significantly around an average value of 0.24, showing that the overall reaction rate increases with the increasing pressure. Since they are the sum of the partial reaction orders with respect to fuel and oxygen, the result is in agreement with the findings reported by previous studies on the catalytic combustion of alkane/air mixtures, which indicate a fuel reaction order $n_F \approx 1$ and negative reaction orders for oxygen, due to the inhibiting effect resulted from its excess adsorption on platinum surface.[12]

1.20% n-hexane/air $r_R = a \cdot p_0^b \cdot \exp(-c/T_w)$
$r^2 = 0.980$; $F_{stat} = 780$
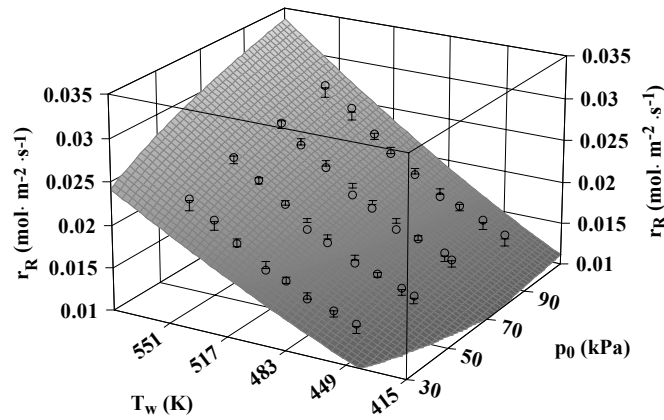**a = 0.150±0.016; b = 0.255±0.017; c = 1577±43**

Fig. 2 – A 3D nonlinear regression analysis $r_R^* = f_1(p_0, T_w)$.

Table 3

Estimated parameters and coefficients of determination r^2
from the nonlinear regression analysis of equations (3) and (4)

% Fuel	1.20	1.50	1.80	2.16
n_1	0.255±0.016	0.254±0.008	0.171±0.009	0.192±0.003
$E_{a,*}$(kJ/mol)	13.10±0.36	12.00±0.27	11.44±0.21	11.58±0.09
α_1	0.150±0.016	0.127±0.009	0.160±0.009	0.154±0.004
r^2	0.980	0.986	0.989	0.998
n_2	0.259±0.044	0.280±0.058	0.250±0.071	0.277±0.031
$E_{a,ind}$(kJ/mol)	89.3±2.8	89.2±6.4	111.4±10.2	121.2±5.3
α_2	(2.39±1.43)e-10	(4.78±7.85)e-10	(1.11±3.03)e-12	(1.02±1.43)e-13
r^2	0.990	0.944	0.918	0.981

Within the limits of experimental errors, the small overall activation energies, $E_{a,*}$, are independent of fuel concentration and are characteristic for the mass transfer processes occurring across the diffusion layer,[10] confirming a small temperature sensitivity of the reaction rate. On the other hand, the overall activation energies evaluated from the induction periods are much higher and are characteristic for kinetically controlled processes. They exhibit a significant increase when the fuel concentration increases, a trend difficult to explain within the framework of the single-step model.

The significance of the activation energy for the mass-transfer controlled process can be understood with the reference to a simplified model which takes into account two steps: the diffusion of fuel molecules to the catalyst surface and an overall single-step surface catalytic reaction.[10] For very short induction periods (characteristic for higher temperatures), the reaction rate follows a saturation-type exponential increase of the form:[10]

$$r_R = a_1 + b_1 \cdot (1 - \exp(-c \cdot t)) \qquad (5)$$

where a_1 is a small term associated with the noise of the measurement, $b_1 = k_D \cdot k_r \cdot C_{V,F}^0 / (k_D + k_r)$, $c = (k_D + k_r)/\phi$ where $k_D = D_F/\delta$ is the rate constant of the diffusion process dependent on the diffusion coefficient D_F of the fuel and on the thickness of the diffusion layer δ, k_r is the overall reaction rate constant, $C_{V,F}^0$ is the volume concentration of the fuel and ϕ is the thickness of a monomolecular layer of fuel molecules in contact with the catalyst surface. For longer induction periods the dependence is shifted to the right along the time axis by the magnitude of τ_{ind}.

For large time values equation (5) reduces to $r_R^* = a_1 + k_D \cdot k_r \cdot C_{V,F}^0 / (k_D + k_r)$ and for $k_r \gg k_D$ becomes: $r_R^* = a_1 + k_D \cdot C_{V,F}^0$, when the overall process is diffusion controlled, with small activation energy. The measured reaction rates can

be compared with the molar collision frequency of the fuel molecules, v_F calculated as $v_F = p_F/(2\pi M_F R T_w)^{1/2}$. For the stoichiometric mixture at $T_w = 549$ K and $p_0 = 101$ kPa the result is $v_F = 43.5$ mol m^{-2} s^{-1} and $r_R^*/v_F = 6.76 \cdot 10^{-4}$ suggesting a low collision efficiency. The derived turnover frequency calculated for the atomic surface density of platinum exposed atoms ($\Gamma_{Pt} = 2.49 \times 10^{-5}$ mol m^{-2}) is $TOF = 1180$ s^{-1}, lower than for the stoichiometric ethane/air mixture[13] in the same conditions ($TOF = 3070$ s^{-1}).

On the other hand, the initial exponential increase of the reaction rate has been attributed to the multiplication of the surface intermediates, analogous to the branching chain mechanism.[16] Taking into account the quasi-equilibrated adsorption-desorption of the oxygen, the one-sided dissociative adsorption of the fuel, the reaction of the adsorbed fuel and oxygen leading either to the multiplication of the adsorbed intermediates or to their conversion into the reaction products, the following kinetic equation proved to describe adequately the experimental results:[16]

$$r_R = [k_a \cdot k_r \cdot C_{V,F}^0 \cdot \phi/(k_m - k_r)] \cdot (\exp((k_m - k_r) \cdot t) - 1)$$

$$(6)$$

where k_a, k_r and k_m stand for the rate constants of fuel adsorption, reaction leading to final products and intermediate multiplication, respectively. The Arrhenius-type temperature dependence of these rate constants and their possible variations with fuel concentration can serve as a basis for the evaluation of the overall activation energy variation reported in Table 3.

EXPERIMENTAL

The experimental data have been carried out using the equipment and procedures described in details in several previous papers.[9-16] The employed method relies on the temporal response of the heterogeneous catalytic reaction following a quasi-rectangular temperature jump applied to a thin platinum wire located in the geometrical center of a test cell. The wire is an arm of a Wheatstone bridge connected to an electronic thermostating circuit.[9] The essential feature of the method consists in the measurement of an exothermic reaction rate of a heterogeneous catalytic reaction in isothermal conditions. The fuel/air mixtures have been prepared using the partial pressures method.[14]

CONCLUSIONS

The catalytic combustion of lean and stoichiometric *n*-hexane/air mixtures on a thin platinum wire have been studied in isothermal conditions at different pressures between 20 and 101 kPa. The reaction rates of the heterogeneous catalytic reaction have been measured for both transient and steady-state regimes. The kinetically controlled transient regime characterizes the ignition process and allows for the measurement of the induction periods. Using an overall single-step reaction model, the overall reaction orders and activation energies have been evaluated from the pressure and temperature variation of the induction periods. The overall reaction order fluctuates around 0.24 reflecting the inhibitory effect of oxygen resulted from its excess adsorption on platinum. The corresponding activation energies have typical values for kinetically controlled processes. The steady state combustion occurs as a diffusion controlled process.

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