



IGNITION OF CATALYTIC OXIDATION OF ETHANOL IN OSCILLATORY REGIME

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The overall activation energy for the ignition of thermokinetic oscillations observed during the heterogeneous catalytic oxidation of ethanol on Pd/Al₂O₃ was obtained and discussed in terms of a PdO_x redox cycle.

INTRODUCTION

Catalytic reactions provide a variety of non-linear dynamic features because, any heterogeneously catalyzed reaction represents a non-equilibrium system namely a dissipative structure. Concerning the palladium – supported oxidation of ethanol an essential point is that the reaction exhibits relaxation oscillations.^{1,2} In these conditions, the ignition of this reaction becomes important for the understanding of the oscillatory behavior.

Ignition of oscillatory oxidation of lower alcohols on Pd-supported catalysts is an important clue for understanding the catalytic surface reactions, because the catalytic oxidation of ethanol is a reaction that can take place either in the steady state or in the oscillatory regime.¹⁻⁴

The highly exothermic catalytic oxidation of ethanol on Pd/Al₂O₃ was monitored by recording the catalyst temperature T vs the temperature of the reactor T_R . $\Delta T = T - T_R$ correspond either to a steady state of reaction or to the dynamic behavior of the system, e.g. in the case of observed thermokinetic oscillations.

In this paper, we try to obtain more informations related to the ignition of the observed thermokinetic oscillations by focusing our attention not on the

minimum values of the temperature oscillations as before⁵ but on the maximum values of the temperature oscillations that can be also reliably determined. With these values it was possible to obtain other activation energy of ignition for the oxidation of ethanol in oscillatory regime. This approach will be demonstrated by temperature oscillations during the heterogeneously catalyzed oxidation of ethanol on Pd-supported catalysts. The dynamic calorimeter, the equipment and experimental conditions have been described earlier.¹⁻⁶

THE MODEL

One period of a temperature oscillation is characterized by two points: a minimum point where the temperature is T_{min} and the maximum of the amplitude where the temperature is T_{max} (Fig. 1).

A regular oscillation can be regarded as to begin not only from the lower point, where $T = T_{min}$ but also from the upper part where $T = T_{max}$. In these conditions the oscillation is $T_{max} \rightarrow T_{min} \rightarrow T_{max}$.

Starting with this point of view the ignition activation energy of the oscillatory oxidation of ethanol on supported Pd-catalysts was determined. For this purpose we have used a formula given by Hiam et al⁷:

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$$\frac{E}{RT_{ig2}} = \ln \left[\frac{n}{(T_{ig2} - T_0)^2} \right] + \ln \left(\frac{QART_0^2}{E\alpha} \right) \quad (1)$$

where T_{ig2} is the temperature of ignition according to Fig. 1, $T_{ig2}=T_{max}$, $T_0=T_R$, the temperature of the

reactor, n = the concentration of reactants Et-OH or O_2 , Q = reaction enthalpy, α =heat transfer coefficient and A =pre-exponential coefficient. T_{ig1} is the temperature when $T=T_{min}$.

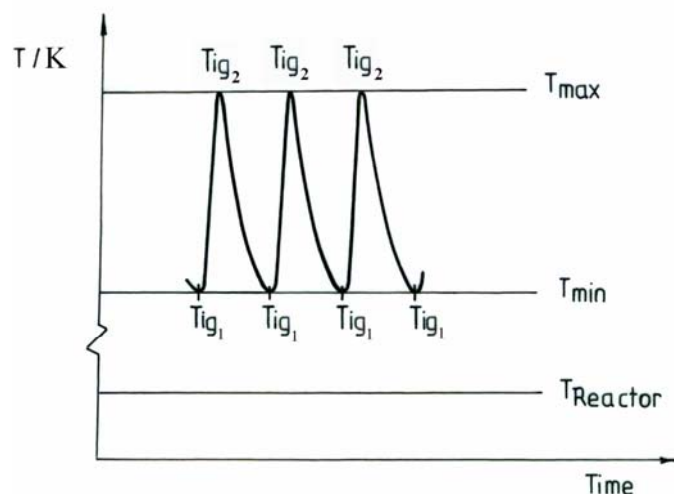


Fig. 1 – Time dependence of temperature oscillations.

Thus a plot $\ln \left[\frac{n}{(T_{ig2} - T_R)^2} \right]$ vs $1/T_{ig2}$ should

lead to a straight line of slope E_{ig2}/R .

Equation (1) was obtained⁷ for a surface reaction of first order in hydrocarbon and zero order in oxygen. We assume that due to the experimental conditions in which the oxidation reaction was performed in conditions in which either the concentration of Et-OH or of O_2 has been changed, the other component of the feed remaining constant, this formula can be applied in our case too.

RESULTS AND DISCUSSION

The ignition temperature of oscillations was obtained from bifurcation diagrams²⁻⁴ in two separate experimental conditions in which either the influence of oxygen or of ethanol concentrations upon the reaction rate was observed *via* the difference in temperature $T-T_R$. The maximum temperature T_{max} , when we have considered this point as the starting point of the oscillation and the minimum temperature T_{min} attain by the oscillation were determined independently of the direction of increasing or

decreasing the oxygen or ethanol concentrations in the feed, the other reactant remaining constant. The results of these measurements were analyzed graphically in Fig. 2 and Fig. 3. From the slope of these lines the activation energy for the catalytic ignition of the oscillations was computed. In the same manner the activation energy of ignition starting the oscillation from the minimum temperature T_{min} was also obtained.⁵

When the ethanol concentration was varied and the oxygen concentration was kept constant, the activation energy of ignition E_{ig2} was 22.3 ± 1.5 (kJ/mol). When the oxygen concentration was changed at a constant concentration of ethanol, the activation energy of ignition was found to be 34.0 ± 1.9 (kJ/mol) (Figs. 2,3).

These values suggest that there are small differences in the activation energy of ignition for a temperature oscillation which starts from T_{max} to T_{min} , depending of the changing parameter ethanol or oxygen.

The results could be qualitatively explained by assuming a PdO_x ($0 < x \leq 1$) redox cycle.⁸⁻⁹ In the high temperature range (T_{max}) the heated surface of Pd clusters becomes progressively oxidized to PdO_x . Due to oxidation of the metal surface, the reactivity drops, the temperature decreases and reaches the lowest point T_{min} . On the oxidized

surface the oxygen sticking coefficient should be very small. At this point the oxide surface will be reduced by ethanol until enough Pd empty sites become available and the dissociative adsorption

of alcohol as the first step of the reaction becomes possible as described for C_1 - C_4 alcohols on platinum metals.¹⁰ The temperature increases and the high temperature point T_{max} is reached again.

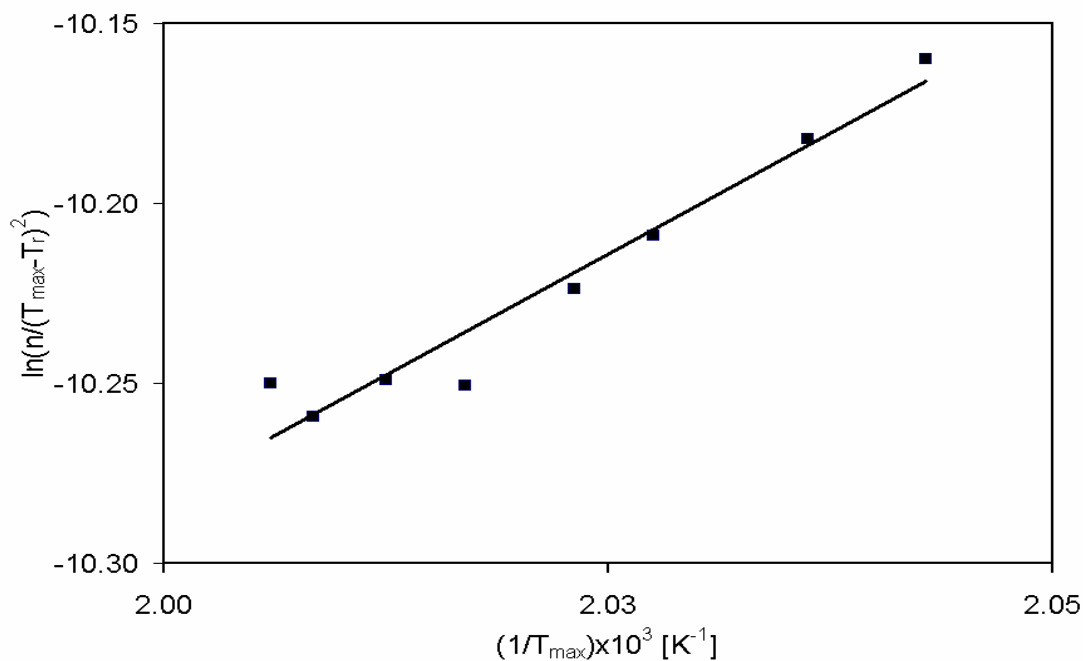


Fig. 2 – Determination of ignition activation energy in case of constant oxygen concentrations. Experimental conditions: $T_R=419.2$ K, 27.8 mg catalyst, 14.7% vol % oxygen, between 3 and 6 vol % ethanol.

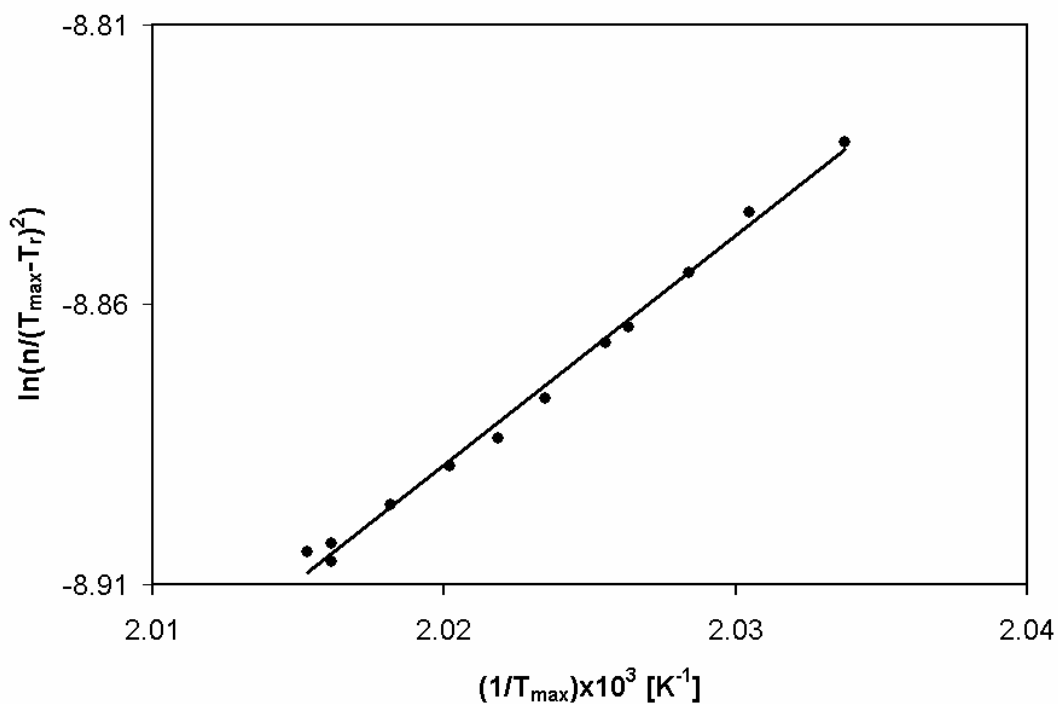


Fig. 3 – Determination of ignition activation energy in case of constant ethanol concentration. Experimental conditions: $T_R=419.2$ K, 27.6 mg catalyst, 4.01 vol% ethanol, between 9 and 18 vol% oxygen.

The decomposition mechanism of C₁-C₄ alcohols on platinum group metals^{10,11} shows that ethanol dissociates, the several C-O and C-H bonds being split. This splitting depends on the type of interaction with the catalyst and the reactions conditions. On palladium the first step of reaction is the dissociative adsorption^{1,10} with the formation of an ethoxy species. Through several consecutive reactions of dehydrogenation and oxidation, with CO and H₂ as intermediates, as in case of methanol^{9,12,13} one obtains the final products CO₂ and H₂O.^{2,3} This happened in case of these oscillations too, where only CO₂ and H₂O are determined.²⁻⁴ The obtained energy of ignition is needed for attaining the critical concentration of reactants and for the ignition of two oxidation reactions namely the oxidations of CO and H₂.⁵ These oxidation reactions take place as long as the Pd free sites necessary for the dissociative adsorption of oxygen and ethanol are available. They disappear due to the formation of PdO_x^{4,5} in the redox cycle. The oxidation (blocking) - reduction (reactivating) surface process is assumed to be the driving force for the oscillations.^{14,15}

In the same time the subsurface oxygen formation cannot be neglected and can give rise to the oscillatory behavior. If the surface is covered by an adsorbed species like CO becoming inactive then the subsurface oxygen reservoir is depleted through segregation to the surface, followed by the oxidation reaction of CO. Thus the catalytic activity of Pd is restored.¹⁶ With the active surface being covered by oxygen the filling of the subsurface oxygen reservoir begins again, completing the oscillatory cycle. Experimental evidence for supported Pd catalysts were provided by X-ray absorption spectroscopy.⁸

The values of activation energies of ignition, starting from T_{max} are similar with the activation energies of oscillations which were around 35 (kJ/mol) in both cases when Et-OH or O₂ are variable.^{3,4} The value of activation energy of 35 (kJ/mol) was obtained using the same bifurcation diagrams, but computing the data with a non-isothermal kinetics and considering the points T_{max} and T_{min} .^{3,4}

On both branches of an oscillation different phenomena occur. On the decreasing branch from T_{max} to T_{min} adsorption of reactants and surface oxidation of Pd occur. From T_{min} to T_{max} the oxidation

of intermediates and surface reduction of PdO_x occur obtaining the final products CO₂ and H₂O.²

These activation energies of ignition cannot be attributed to a single rate determining step, because the processes of obtaining the intermediates and products will be quite complex only the combination of all reaction steps yields on overall activation energy of ignition for a lumped system that we are not able to model at the present time.

CONCLUSIONS

The overall activation energy of ignition for the catalytic oxidation of ethanol on a Pd/Al₂O₃ catalyst in oscillatory regime was determined using the maximum values of temperature oscillations. The obtained values are similar with the overall activation energies of the corresponding thermokinetic oscillations.

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