

Dedicated to Professor Victor-Emanuel Sahini
on the occasion of his 80th anniversary

OVERALL ACTIVATION ENERGY OF METHANOL OXIDATION IN OSCILLATORY REGIME

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The thermokinetic oscillations obtained in a dynamic calorimeter during the heterogeneous catalytic oxidation of methanol on a palladium supported catalyst were characterized by overall activation energy. This parameter was determined by using the minimum and maximum values of the temperature oscillations. By using the individual thermokinetic oscillations and a bifurcation diagram in which the oxygen content in the feed was only increased, the E values for all three heating loss laws were calculated. The results have been discussed in terms of a redox cycle of the palladium supported catalyst.

INTRODUCTION

The oscillatory behavior of heterogeneous catalytic oxidation of methanol on supported palladium catalysts is now well established.¹⁻¹²

$\Delta T = T - T_R$ represents the difference between the catalyst temperature T and the temperature of the reactor T_R either for the reaction in steady state conditions or in dynamic conditions (*i.e.* in the case of observed thermokinetic oscillations).

In our previous papers¹¹⁻¹⁴ the temperature oscillations were considered as the result of a non-isothermal process in which the necessary energy for the thermokinetic oscillations is provided not from outside, but from inside of the system, by the exothermal process of oxidation itself.

Using the minimum and the maximum values of the temperature oscillations, we obtained a heat balance equation. With this model and with the bifurcation diagrams or series of thermokinetic oscillations, we were able to obtain the overall activation energy of a heterogeneous catalytic reaction in oscillatory regime. In the bifurcation diagrams methanol or oxygen were the bifurcation parameters,^{11, 12} these parameters being changed

not only in one direction of variation but also in the opposite one.

In this paper we try to verify the model and to obtain the overall activation energy of one thermokinetic oscillation. Also, we will use bifurcation diagrams in which the oxygen concentration, the bifurcation parameter, is changed only in one direction of variation.

This approach will be demonstrated by analyzing the temperature oscillations during the heterogeneously catalysed oxidation of methanol on a Pd/LiAl₅O₈ (Bayer), the equipment and the experimental conditions being described earlier.^{5,7}

THE MODEL

In a real system part of the heat developed in an exothermal reaction produces the temperature increase and another part of it is lost to the environment by heat transfer processes.

The heat balance equation of an exothermal reaction at a spatially uniform temperature, in which the heat transfer coefficient is assumed to be temperature independent, is given by:

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$$mc \frac{dT}{dt} = -\Delta H \cdot r - hA(T - T_R) \quad (1)$$

where m and c represent the mass and the specific heat of the catalyst, ΔH is the reaction enthalpy, h is the heat transfer coefficient at the surface of the catalyst of surface area A , $T - T_R$ is the difference between the catalyst temperature T and the temperature of the reactor T_R and r is the overall reaction rate. In Eq. (1) the generation of chemical energy compensates the heat loss of the catalyst due to the gas flow, the heating energy of the reactant gas being neglected.

Dividing Eq.(1) by mc and using the notations $-\frac{\Delta H}{mc} = \alpha$ and $\frac{hA}{mc} = K$ (cooling coefficient), the heat balance becomes:

$$\frac{dT}{dt} = \alpha r - K(T - T_R) \quad (2)$$

As the curves of temperature variations are characteristic for non-isothermal processes, a law of non-isothermal kinetics¹⁵ can be applied. In this case the overall reaction rate r can be written as a product of two functions, one depending only on temperature and the other on concentration:

$$r = k(T) f(c) \quad (3)$$

where the function $f(c)$ describes the concentration dependent dynamics of the reactants.

Using now some usual assumptions concerning the function $k(T)$ and taking into account that the heat transfer coefficient can be either temperature independent¹³ or dependent^{16,17} one obtains the

following relations for the overall activation energy:

$$E = R \frac{T_{\max} \cdot T_{\min}}{T_{\max} - T_{\min}} \ln \left(\frac{\Delta T_{\max}}{\Delta T_{\min}} \right) \quad (4)$$

when the heat transfer coefficient is temperature independent¹³ (the case of conduction),

$$E = R \frac{T_{\max} \cdot T_{\min}}{T_{\max} - T_{\min}} \cdot \frac{5}{4} \ln \left(\frac{\Delta T_{\max}}{\Delta T_{\min}} \right) \quad (5)$$

when the heat transfer coefficient is temperature dependent in case of free convection^{11,16,17} and

$$E = R \frac{T_{\max} \cdot T_{\min}}{T_{\max} - T_{\min}} \cdot \ln \left(\frac{T_{\max}^4 - T_R^4}{T_{\min}^4 - T_R^4} \right) \quad (6)$$

in case of radiation energy loss^{11,16,17}. In Eqs. (4) – (6) T_{\max} and T_{\min} are the maximum and minimum values of a temperature oscillation respectively.

RESULTS AND DISCUSSION

a) Individual oscillations

The thermokinetic oscillations obtained in the catalytic oxidation of methanol with oxygen are presented in Figs. 1 and 2. At favorable pre-established conditions, the reaction enters just from the beginning in the oscillatory regime. These figures describe the influence of different oxygen and methanol concentrations on the temperature increase observed via the differences ΔT .

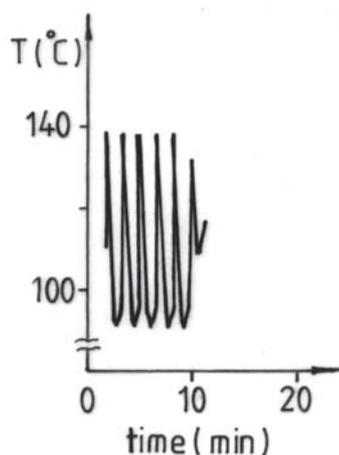


Fig. 1 – The amplitude of thermokinetic oscillations. Experimental conditions: 18 mg catalyst Bayer (Pd/LiAl₅O₈), temperature of the reaction cell 80°C, methanol content 5.0% vol., oxygen flow rate 5.8 mL·min⁻¹.

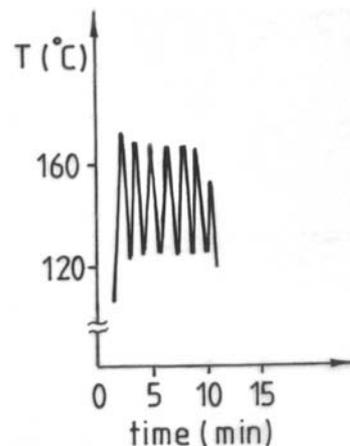


Fig. 2 – Amplitude of thermokinetic oscillations. Experimental conditions: 20mg catalyst Bayer (Pd/LiAl₅O₈), temperature of the reaction cell 80°C, methanol content 8.0% vol., oxygen flow rate 7.7 mL·min⁻¹.

By using these ΔT values obtained from Figs. 1 and 2 the overall activation energy of the oscillatory behavior was obtained using Eqs. (4)-(6). These values obtained from Fig. 1 are $E_{T^1} = 44.2 \text{ kJ} \cdot \text{mol}^{-1}$, $E_{T^4} = 49.7 \text{ kJ} \cdot \text{mol}^{-1}$ and $E_{T^{5/4}} = 55.2 \text{ kJ} \cdot \text{mol}^{-1}$. E_{T^1} , E_{T^4} and $E_{T^{5/4}}$ are overall activation energies in the cases of a conduction, a radiation and a convection heat loss law respectively, the highest values being obtained in the case of free convection loss as in some other previous experiments.^{11,14} From Fig. 2 the same values are: $E_{T^1} = 22.7 \text{ kJ} \cdot \text{mol}^{-1}$, $E_{T^4} = 28.8 \text{ kJ} \cdot \text{mol}^{-1}$, and $E_{T^{5/4}} = 28.4 \text{ kJ} \cdot \text{mol}^{-1}$. These differences obtained in the values of the overall activation energies in the two cases represented in Fig. 1 and Fig. 2 can be attributed to the different experimental conditions in both experiments i.e. the oxygen feed rate of 5.8 mL/min and 7.7 mL/min, respectively.

b) Bifurcation diagram

A bifurcation diagram records the qualitative changes in the dynamic behavior of a system depending upon the experimental parameters, e.g. the transformation of a steady state into an oscillatory one.

The bifurcation diagram shown in Fig. 3 describes the influence of the oxygen concentration upon the reaction rate observed via the increase of temperature T . The stable states in Fig. 3 are represented by the full line whereas the oscillations are indicated by the vertical lines representing the amplitude of the oscillations. In this case the bifurcation parameter oxygen concentration was changed only in the direction of increasing the flow rate and not in both increasing/decreasing direction as reported previously.¹⁰⁻¹⁴

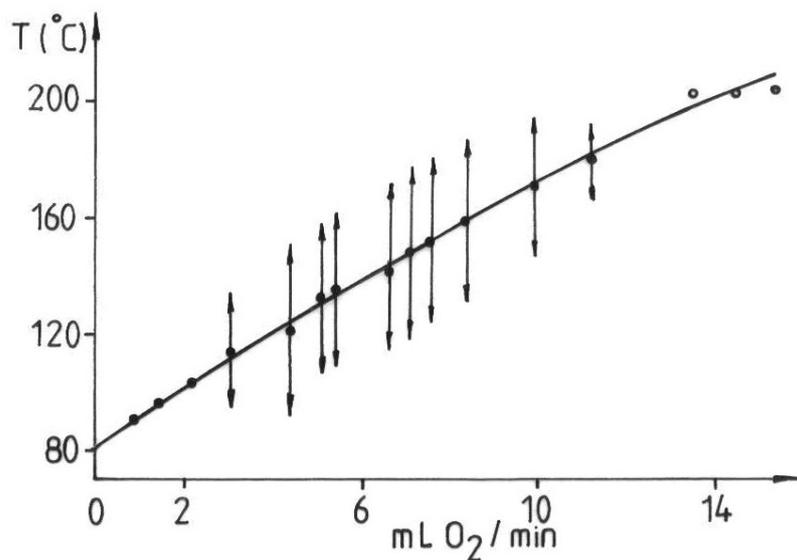


Fig. 3 – Bifurcation diagram: temperature increase of the catalyst bed ($\text{Pd/LiAl}_5\text{O}_8$), vs oxygen content in the feed ($T_R = 80^\circ\text{C}$, 20 mg catalyst, methanol in the feed 5.0%). The oxygen content in the feed is only increased.

At low oxygen content only stable steady states were observed. On increasing the oxygen concentration on in the feed in A there is a transition to a stable oscillatory state. As shown, with the increase of oxygen concentration in feed, the amplitude of oscillations increases and then, after a while, decreases to point B where they disappear. The point B represents a new transition from a stable oscillatory state to a stable steady state.

By using the ΔT values obtained from Fig. 3 the overall activation energy values of the oscillatory behavior were determined as a function of oxygen content in the feed (Eqs. 4-6).

For the bifurcation diagram two linear dependencies of the oxygen content were obtained for all the three cases for the heat lost. The intersecting point of the straight lines is situated around 7.0 mL O_2 /min (Fig. 4) in all cases.

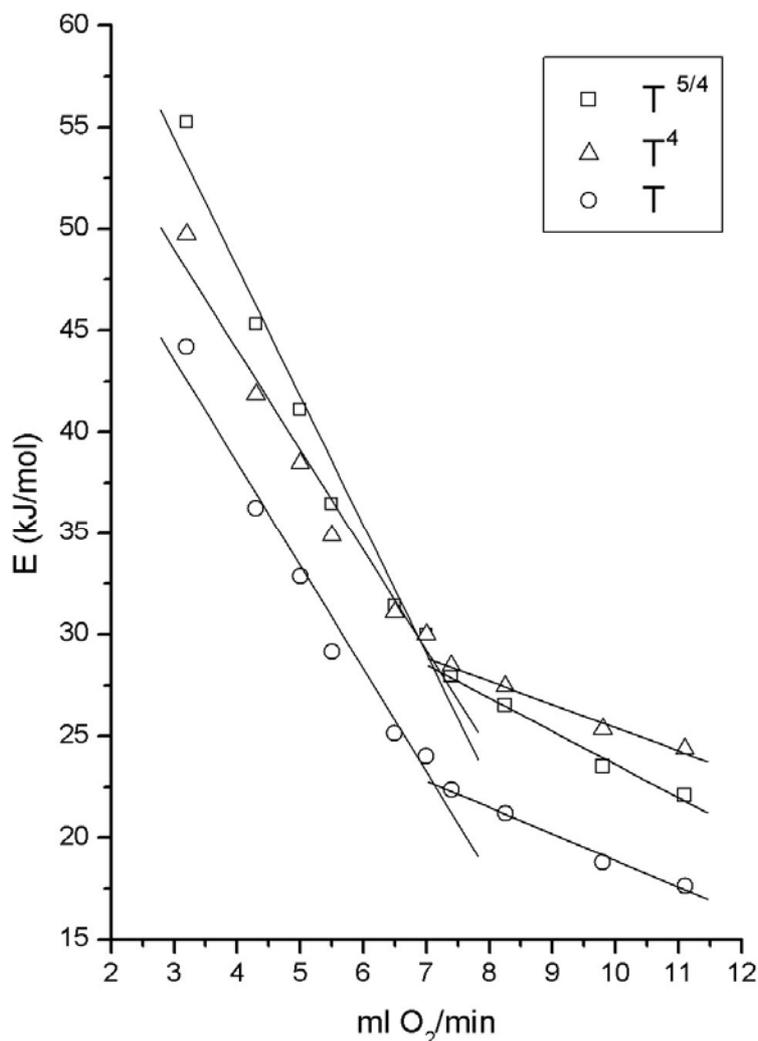


Fig. 4 – Overall activation energy vs oxygen content in the feed.

For the first straight line, in the range from 3.2 to 7.0 mL O₂ min⁻¹ the values of the overall activation energy are ranging between 44.2 kJ mol⁻¹ and 24.0 kJ mol⁻¹ in the case when the heat loss occurs by conduction, between 49.7 kJ mol⁻¹ and 30.0 kJ mol⁻¹ in the case of radiation and between 55.3 kJ mol⁻¹ and 30.0 kJ mol⁻¹ in the case of free convection. For the second line the values are comprised between 22.4 – 17.7 kJ mol⁻¹ for conduction, 28.5-24.4 kJ mol⁻¹ for radiation and 28.0 – 22.1 kJ mol⁻¹ for free convection.

These values are within the range of activation energies known for heterogeneous catalytic oxidation reactions.¹⁸

c) General discussion

Two intersecting straight lines were also obtained previously for methanol oxidation in oscillatory regime when for the determination of the overall activation energies were used the

bifurcation diagrams obtained by increasing and decreasing the oxygen content in the feed¹¹. Two intersecting straight lines were also obtained in case of a series of thermokinetic oscillations of methanol when the oxygen concentration was only increased¹² in the feed. Such behavior was already observed also in the case of ethanol oxidation.^{13,14}

The existence of two intersecting straight lines for the overall activation energy could be an indication for the presence of two different pathways for the oscillatory oxidation of methanol on a palladium supported catalyst. These mechanisms could exist simultaneously on the surface and only the reaction conditions make one or another mechanism to prevail.

Methanol adsorption on Pd occurs dissociatively¹⁹ as reported for C₁-C₄ alcohols on platinum metals^{20,21}. Passing through several consecutive reactions of dehydrogenation and oxidation (with CO and H₂ as intermediates^{20,22}) one obtains CO₂ and H₂O as final products⁹ as in the case of oscillations analysed here.

The present results can be qualitatively explained by assuming a redox cycle of the palladium catalyst.²³⁻²⁵ In the high temperature range the heated Pd surface becomes progressively oxidized to PdO_x with $0 < x \leq 1$, because the high local temperature of the Pd particles provides a good condition for their oxidation to PdO_x.

Due to the oxidation of the active metal surface, the reactivity drops, the temperature decreases and reaches the lowest value of active Pd T_{min}. At this point the oxide surface will be reduced by the alcohol, which was previously adsorbed in these conditions. The reaction attains the critical conditions level and the CO and H₂ resulted from methanol will react with PdO_x leading to CO₂ and H₂O both reactions being exothermal. The temperature increases during this step and the high temperature with a maximum temperature T_{max} is reached again. A new oscillation can start. This model represents a nonisothermal surface blocking/reactivating mechanism assuming a Langmuir-Hinshelwood type reaction kinetics. The oxidation (blocking) – reduction (reactivating) process is assumed to be the driving force for oscillations.²⁶⁻²⁹

CONCLUSIONS

The overall activation energy of methanol oxidation on a palladium supported catalyst in oscillatory regime was determined for some individual thermokinetic oscillations by using the minimum and maximum values of the temperature oscillations. This energy was also determined by using a bifurcation diagram in which the oxygen content in the feed was only increased. It was shown that apparently there are two surface mechanisms responsible for the oscillatory behavior.

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