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TEMPERATURE OSCILLATIONS CHARACTERIZED BY AN OVERALL ACTIVATION ENERGY

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Abstract

Temperature oscillations obtained during the heterogeneous catalytic oxidation of ethanol on Pd–Al_2O_3 in a dynamic calorimeter were characterized by an overall activation energy. This parameter was determined by a non-isothermal kinetic method using the minimum and maximum values of the oscillations temperature. Using the bifurcation diagram with the oxygen as a bifurcation parameter an E value between 27.6 and 28.2 kJ mol^{-1} was obtained. With ethanol as bifurcation parameter the E values lies between 28.1 and 31.1 kJ mol^{-1} for 3.5 to 4.0 vol% ethanol and between 25.8 and 27.6 kJ mol^{-1} for 4.0 to 4.7 vol% ethanol. These results have been discussed.

Keywords: overall activation energy, oxidations, thermokinetic oscillations

Introduction

Oscillations in heterogeneous catalytic system are normally observed on macroscopic scale either as product oscillations in the outlet of the flow reactor or as oscillations of a quantity which is dependent to the product concentration i.e. the temperature variation. The analysis of temperature oscillations is generally restricted to the investigation of the dependence of their amplitude and frequency on the experimental parameters: reaction temperature, concentration of reactants, flow rate of the feed or the amount and geometry of catalyst [1–14].

The highly exothermic catalytic oxidation of ethanol on Pd–Al_2O_3 is monitored by recording the catalyst temperature T *vs.* the temperature of the reactor T_R, $\Delta T=T-T_R$ this corresponds either to a steady state rate of reaction or to the dynamic behaviour of the system, e.g. in the case of observed thermokinetic oscillations [7, 12].

We consider the temperature oscillations like a non-isothermal process in which the necessary energy for the thermokinetic oscillations is brought not from outside, but from inside, by the exothermic process of oxidation itself.

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In this paper, we try to obtain more information related to the mechanism of the observed oscillations by focusing our attention to the minimum and maximum values of oscillations temperature that can be determined unambiguously. With these temperature values and using some assumptions it was possible to obtain the overall activation energy of the heterogeneous catalytic reaction in oscillatory regime. This approach will be demonstrated by analyzing temperature oscillations during the heterogeneously catalyzed oxidation of ethanol on Pd–Al_2O_3 catalyst, the dynamic calorimeter, the equipment and the experimental conditions described earlier [7, 12].

The model

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

$$mc\frac{dT}{dt}=-\Delta Hr-hA(T-T_R) \qquad (1)$$

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

Following a notation introduced by Wicke *et al.* [15], dividing Eq. (1) by mc and using the notations $-\Delta H/(mc)=\alpha$ and $hA/(mc)=K$ (cooling coefficient), the energy balance becomes:

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

In order to apply Eq. (2) in case of an oscillating rate of reaction some comments concerning the overall reaction rate r are necessary. Experimentally observed bifurcation diagrams in case of the catalytic oxidation of ethanol on a Pd supported catalyst [7, 12] reveal the concentration of ethanol and of oxygen, for a given temperature of the reactor T_R as the experimental parameters determining the dynamic behavior of the system as measured by ΔT.

A bifurcation diagram records qualitative changes in the dynamic behavior of a system depending upon the experimental parameters [16] (which could be the bifurcation parameters), e.g. the transformation of a steady state into an oscillatory one. It has to be represented by a proper system of differential equations to obtain the bifurcation diagram, which was experimentally observed [12]. In this case three variables are necessary. The variables which determine the phase space of the system are the concentrations of ethanol c_1 of oxygen c_2 and the temperature T of the oscillation. The reaction rate r will be then a function of these parameters i.e.:

$$r=\frac{\mathrm{d}\phi(c_1,c_2,T)}{\mathrm{d}t} \tag{3}$$

As the temperature variation curves are characteristic for non-isothermal processes we assume that a law of non-isothermal kinetics [17] can be applied. In this case Eq. (3) can be written as a product of two functions, one depending only on temperature and the other one, only on concentrations:

$$r=\frac{\mathrm{d}\phi(c_1,c_2,T)}{\mathrm{d}t}=k(T)f(c) \tag{4}$$

where

$$f(c)=\varphi(c_1, c_2) \tag{5}$$

Function $f(c)$ expresses the dynamic behavior of the reactants of the system in dependence upon concentration.

In such a way the periodic oscillations of temperature in a limit cycle can be described by only one differential equation.

Function $k(T)$ is assumed to have the usual form:

$$k(T)=k_0\exp\left(-\frac{E}{RT}\right) \tag{6}$$

$k(T)$ being a reaction rate constant k_0 the pre-exponential factor and E an activation energy.

One period of a temperature oscillation is characterized by two extrema where $\mathrm{d}T/\mathrm{d}t=0$ one at the minimum point where the temperature is T_{min} , and one at the top where the temperature is T_{max} (Fig. 1)

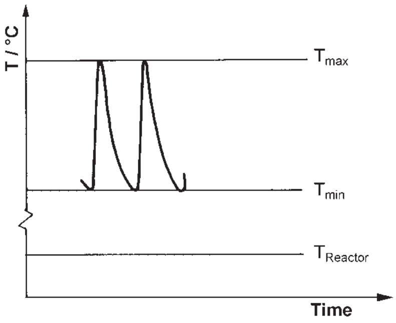

Fig. 1 Time function of temperature oscillations

Taking into account these observations and using Eqs (4) and (6), Eq. (2) reads in two states:

$$\alpha k_0\exp\left(-\frac{E}{RT_{\mathrm{max}}}\right)f(c)_{\mathrm{max}}=K(T_{\mathrm{max}}-T_{\mathrm{R}}) \tag{7}$$

and

$$\alpha k_0 \exp\left(-\frac{E}{RT_{\min}}\right) f(c)_{\min} = K(T_{\min} - T_{\mathrm{R}}) \tag{8}$$

The products of the catalytic oxidation of ethanol in oscillatory regime are CO_2 and H_2O [9]. Also the differences between the values of $T_{\max}$ and $T_{\min}$ are not great. The approach relies on the fact that $\Delta T_{\min/\max} << T - T_{\mathrm{R}}$ or $T_{\max} - T_{\mathrm{R}} \cong T_{\min} - T_{\mathrm{R}}$. It is assumed that in this range the parameter E is temperature independent and the values α, k_0 and K are not affected. Therefore Eq. (7) can be divided by Eq. (8) which leads to:

$$\frac{\exp\left(-\frac{E}{RT_{\max}}\right) f(c)_{\max}}{\exp\left(-\frac{E}{RT_{\min}}\right) f(c)_{\min}} = \frac{T_{\max} - T_{\mathrm{R}}}{T_{\min} - T_{\mathrm{R}}} = \frac{\Delta T_{\max}}{\Delta T_{\min}} \tag{9}$$

or

$$\exp\frac{E}{R}\left[\left(\frac{1}{T_{\min}} - \frac{1}{T_{\max}}\right)\right] \frac{f(c)_{\max}}{f(c)_{\min}} = \frac{\Delta T_{\max}}{\Delta T_{\min}} \tag{10}$$

Equation (10) presents two unknowns: i.e. E and the ratio $f(c)_{\max}/f(c)_{\min}$ There are two possibilities now: either to consider the ratio $f(c)_{\max}/f(c)_{\min} \equiv 1$ and to determine an overall activation energy or to determine the overall activation energy, in the bifurcation point and to use this value in Eq. (10) in order to see the change of the ratio $f(c)_{\max}/f(c)_{\min}$ *vs.* the oxygen or ethanol concentration.

If function $f(c)$ does not change significantly in the range ($T_{\min}$, $T_{\max}$) then:

$$\frac{f(c)_{\max}}{f(c)_{\min}} \equiv 1 \tag{11}$$

With Eq. (11) Eq. (10) becomes:

$$E = R\frac{T_{\max} T_{\min}}{T_{\max} - T_{\min}} \ln\left(\frac{\Delta T_{\max}}{\Delta T_{\min}}\right) \tag{12}$$

In the second case one obtains:

$$\frac{f(c)_{\max}}{f(c)_{\min}} = \exp\left[-\frac{E_0}{R}\left(\frac{1}{T_{\min}} - \frac{1}{T_{\max}}\right)\right] \frac{\Delta T_{\max}}{\Delta T_{\min}} \tag{13}$$

where E_0 is the overall activation energy E in the bifurcation point.

Results and discussion

The results obtained are presented in Figs 2–7.

The bifurcation diagram shown in Fig. 2 describes the influence of the oxygen concentration upon the reaction rate observed via the difference in temperature Δ*T*. The stable states in Fig. 2 are represented by the full line whereas the oscillations are given by vertical lines representing the amplitude of the oscillation.

A bifurcation diagram obtained by using the ethanol content in the feed [9] is presented in Fig. 3.

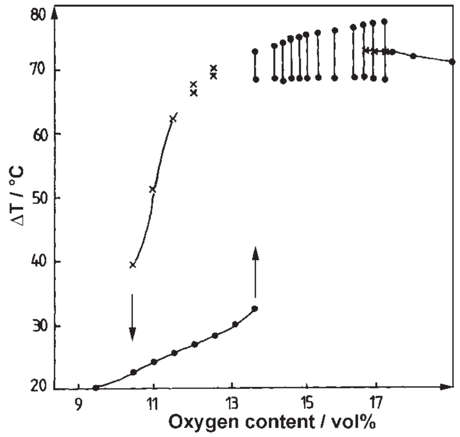

Fig. 2 Bifurcation diagram: temperature difference Δ*T* between the catalyst support and the temperature reactor T_R *vs*. oxygen content in the feed (T_R=146°C, 27.6 mg catalyst, 4.01 vol% ethanol); × – value obtained by decreasing the oxygen content in the feed; • – values of the minimum and maximum temperatures oscillations independently of the sense of increasing and decreasing the oxygen content in the feed

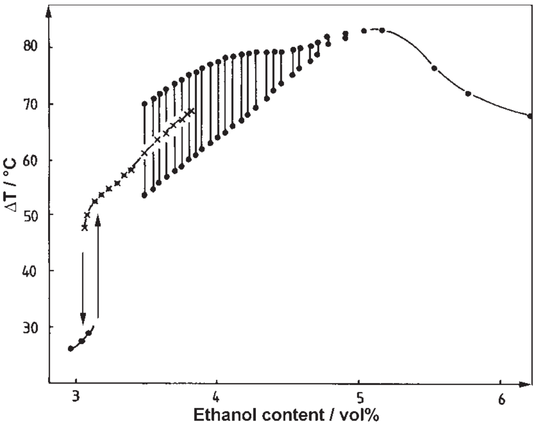

Fig. 3 Bifurcation diagram: temperature difference Δ*T* between the catalyst support and the temperature reactor T_R *vs*. oxygen content in the feed (T_R=146°C, 27.8 mg catalyst, 14.7 vol% oxygen); × – value obtained by decreasing the oxygen content in the feed; • – values of the minimum and maximum temperatures oscillations independently of the sense of increasing and decreasing the ethanol content in the feed

Using the ΔT values obtained from Figs 2 and 3 the overall activation energy of the oscillatory behavior was determined. These energies were obtained by using Eq. (12) under the assumption that $f(c)$ does not change significantly in the range (T_{min}, T_{max}). This assumption is based on the fact that ΔT_{max} and $\Delta T_{min} << T_R$.

For the first bifurcation diagram (Fig. 2) the value of E was determined and lies between 27.6 and 28.2 kJ mol^{-1} (Fig. 4).

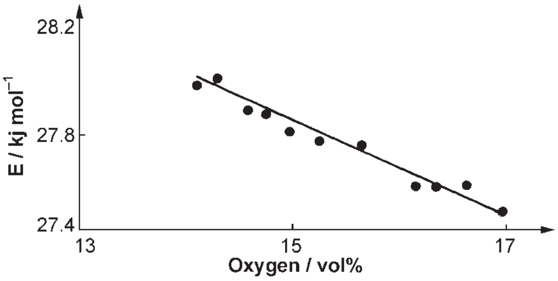

Fig. 4 Parameter E *vs*. oxygen content in the feed

For the second diagram (Fig. 3) two linear dependencies of the overall activation energy upon the ethanol content were observed intersecting in a point situated around 4.0 vol% ethanol (Fig. 5)

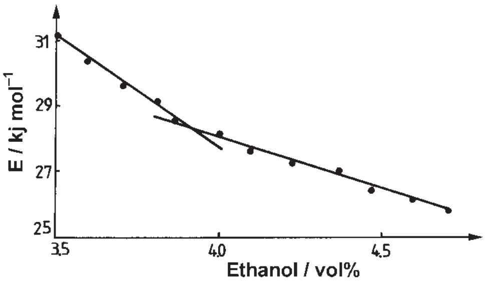

Fig. 5 Parameter E *vs*. ethanol content in the feed

For the first straight line, in the range from 3.5 to 4.0 vol% ethanol the values of activation energy are comprised between 28.1 and 31.1 kJ mol^{-1}, whereas for the second line, in the range from 4.0 to 4.7 vol% ethanol the limits are between 25.8 and 27.6 kJ mol^{-1}.

During one period of oscillation, a large number of diffusion, adsorption, reaction and desorption steps will occur. Moreover, the catalyst itself may undergo changes like oxidation-reduction cycles or adsorbate-induced reconstructions [18]. The sequence of all these processes will be quite complex and this energy can not be attributed to a single rate-determining step. Only the combination of all reaction steps yields an overall Arrhenius energy.

The values obtained are within the range of activation energies for heterogeneous catalytic oxidation reactions [19].

In order to explain this behaviour of the overall activation energy, the concerning hypothesis, i.e. the variation of *f*(*c*) has to be dropped.

From the dependencies ΔT_{osc} *vs.* oxygen or ethanol concentrations, the value E_0 was determined, by extrapolation of E to the bifurcation point. From the dependence ΔT_{osc} *vs.* oxygen the value of E_0 in the bifurcation point is 28.5 kJ mol^{-1}. For the second dependence ΔT_{osc} *vs.* ethanol an E_0 of 25.1 kJ mol^{-1} was determined. With these values the ratios $f(c)_{max}/f(c)_{min}$ *vs.* oxygen respective ethanol concentrations were calculated and are presented in Fig. 6 for oxygen and in Fig. 7 for ethanol. The formula used was Eq. (13).

Figure 6 presents points distributed on a straight line, the maximum difference obtained being 0.004. From this it can be concluded that the function *f*(*c*) does not change significantly in this concentration range.

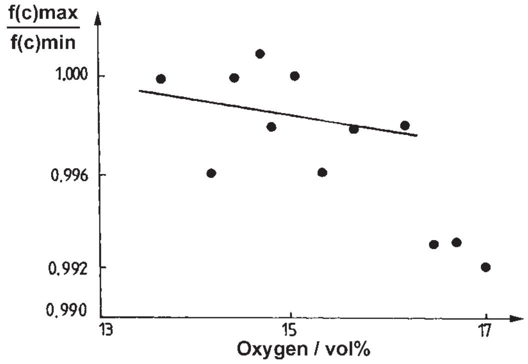

Fig. 6 The ratio $f(c)_{max}/f(c)_{min}$ *vs.* oxygen content in the feed

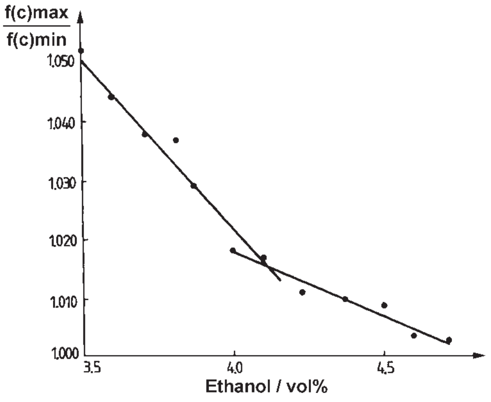

Fig. 7 The ratio $f(c)_{max}/f(c)_{min}$ *vs.* ethanol content in the feed

Figure 7 presents two straight lines, with an intersection point around 4.10 vol% ethanol. The two slopes follow the same behaviour as in Fig. 5.

When oxygen is the bifurcation parameter, $T_{\min}$ remains practically at the same level, as it can be observed in Fig. 2 and when ethanol is the bifurcation parameter, $T_{\min}$ increases with ethanol content as it can be observed in Fig. 3.

The values of the ratio $f(c)_{\max}/f(c)_{\min}$ and of the overall activation energy E represented by the first straight lines of Figs 5 and 7 are the points, where, starting the experiments with the variation of bifurcation parameter ethanol from small content of ethanol, no oscillations occur. The second straight lines of these figures are located in a range of ethanol concentrations where oscillations occur independently of experiment sense, i.e. increasing or decreasing the ethanol concentration.

As it can be seen in Fig. 6 there are three points which do not belong to the straight line. These are exactly the points, where, coming back with the experiment of oxygen as bifurcation parameter, oscillations do not occur.

From Figs 6 and 7 it can be concluded that the overall activation energies of oscillating reactions must be determined in ranges where only stable limit cycles occur in the bifurcations diagrams independently of the experiment sense.

Conclusions

A suitable method to investigate the oscillating reaction of ethanol oxidation on palladium, was developed using the temperature oscillations. This method could be used in analyzing other thermokinetic oscillations too.

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