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ROLE OF THE HEAT-TRANSFER COEFFICIENT IN DETERMINING THE OVERALL ACTIVATION ENERGY OF THERMOKINETIC OSCILLATIONS

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Abstract

Thermokinetic oscillations obtained during the heterogeneous catalytic oxidation of methanol on Pd/$LiAl_5O_8$ in a dynamic calorimeter were characterized by an overall activation energy. This parameter was determined using the minimum and maximum values of the temperature oscillations. Using bifurcation diagrams with oxygen or methanol as bifurcation parameters. *E* values for all heating loss laws were calculated which are within the range for heterogeneous catalytic oxidation reactions. The obtained results have been discussed.

Keywords: heat loss, overall activation energy, thermokinetic oscillations

Introduction

Oscillatory behavior of the heterogeneous catalytic oxidation of methanol on supported palladium catalysts is now well established [1–9].

The highly exothermic catalytic oxidation of methanol on Pd/$LiAl_5O_8$ (Bayer) was 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 behavior of the system, e.g. in the case of observed thermokinetic oscillations.

In a previous paper [10] we have considered 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. Using the minimum and maximum values of the oscillations temperature we have obtained a heat balance equation in which the heat-transfer coefficient was assumed to be temperature independent. With this model we were able to obtain the overall activation energy of a heterogeneous catalytic reactions in oscillatory regime [10].

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In this paper we try to obtain more informations related to the overall activation energy in cases when the heat-transfer coefficient is assumed to be temperature dependent.

This approach will be demonstrated by analyzing temperature oscillations during the heterogeneously catalysed oxidation of methanol on Pd/$LiAl_5O_8$ catalyst (Bayer) the dynamic calorimeter, the equipment and the experimental conditions being described earlier [5, 6, 9].

The model

In our real system a proportion of the developed heat is used to raise the temperature measured by a system of thermocouples [6] and there are losses to the environment due to heat transfer processes.

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:

$$mc\frac{\mathrm{d}T}{\mathrm{d}t}=-\Delta Hr-hA(T-T_{\mathrm{R}}) \tag{1}$$

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), $T–T_{\mathrm{R}}$ 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.* [11], dividing Eq. (1) by mc and using the notations $-\frac{\Delta H}{mc}=\alpha$ and $\frac{hA}{mc}=K$ (cooling coefficient), the energy balance becomes:

$$\frac{\mathrm{d}T}{\mathrm{d}t}=\alpha r-K(T-T_{\mathrm{R}}) \tag{2}$$

Important forms of temperature dependence of the heat transfer are free convection and radiation [12–14]. These cases, with a physical sense, have to be taken into consideration when the heat loss is not a Newtonian one.

In the first case, the free convection, the heat transfer coefficient is proportional to $(T–T_{\mathrm{R}})^{1/4}$ and in the second case, the radiative one, the heat losses is proportional to T^4-T_{R}^4 [12, 13]. These dependencies were given for a point ignition of a reaction in gases. In our cases we can apply these models because the volume of the sample (20 mg catalyst) can be considered as a point of ignition and can be neglected in comparison with the volume of the dynamic calorimeter (some tenth mL)

Taking into account the free convection, Eq. (2) becomes:

$$\frac{\mathrm{d}T}{\mathrm{d}t}=\alpha r-\chi(T-T_{\mathrm{R}})^{5/4} \tag{3}$$

where χ is the new constant.

In case of radiative heat transfer the term $K(T–T_R)$ in Eq. (2) has to be replaced by $\beta(T^4 - T_R^4)$ and the equation takes the form:

$$\frac{dT}{dt} = \alpha r - \beta(T^4 - T_R^4) \tag{4}$$

where β is an other constant.

In order to apply Eqs (2)–(4) in case of an oscillating rate of reactions some comments concerning the overall reaction rate r are necessary. Experimentally observed bifurcation diagrams in case of catalytic oxidation of methanol on a Pd supported catalyst [9] reveal the concentration of alcohol and 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 [15] (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 [9]. In this case three variables are necessary. The variables which determine the phase space of the system are the concentrations of methanol c_1, of oxygen c_2 and the temperature T of the oscillations. The reaction rate r will be then a function of these parameters i.e.:

$$r = \frac{d\phi(c_1, c_2, T)}{dt} \tag{5}$$

As the temperature variation curves are characteristic for non-isothermal processes we assume that a law of non-isothermal kinetics [16] can be applied. In this case Eq. (5) can be written as a product of two functions, one depending only on temperature and the other one, only on concentrations:

$$r = \frac{d\phi(c_1, c_2, T)}{dt} = k(T) f(c) \tag{6}$$

where

$$f(c) = \phi(c_1, c_2) \tag{7}$$

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

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

$$k(T) = k_0 \exp\left(-\frac{E}{RT}\right) \tag{8}$$

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

As previously reported [10] one period of a temperature oscillation is characterized by two extrema where dT/dt=0 one at the minimum point where the temperature is $T_{\min}$ and one at the top where the temperature is $T_{\max}$.

Taking into account these observations and using Eqs (6) and (8), Eq. (3) reads in the two states:

$$\alpha k_0 \exp\left(-\frac{E}{RT_{\max}}\right) f(c)_{\max} = \chi (T_{\max} - T_{\mathrm{R}})^{5/4} \tag{9}$$

and

$$\alpha k_0 \exp\left(-\frac{E}{RT_{\min}}\right) f(c)_{\min} = \chi (T_{\min} - T_{\mathrm{R}})^{5/4} \tag{10}$$

It is assumed that in the range ($T_{\min}$, $T_{\max}$) the parameter E is temperature independent and the values α, k_{o} and χ are not affected. Therefore Eq. (9) can be divided by Eq. (10) which leads to:

$$\exp\frac{E}{R}\left[\left(\frac{1}{T_{\min}} - \frac{1}{T_{\max}}\right)\right]\frac{f(c)_{\max}}{f(c)_{\min}} = \left(\frac{T_{\max} - T_{\mathrm{R}}}{T_{\min} - T_{\mathrm{R}}}\right)^{5/4} = \left(\frac{\Delta T_{\max}}{\Delta T_{\min}}\right)^{5/4} \tag{11}$$

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

$$\frac{f(c)_{\max}}{f(c)_{\min}} \cong 1 \tag{12}$$

With Eq. (12) Eq. (11) becomes:

$$E = R\frac{T_{\max} T_{\min}}{(T_{\max} - T_{\min})}\frac{5}{4}\ln\left(\frac{\Delta T_{\max}}{\Delta T_{\min}}\right) \tag{13}$$

Using the same reasoning as before, in case of radiation loss, (Eq. (4)) the overall activation energy becomes:

$$E = R\frac{T_{\max} T_{\min}}{(T_{\max} - T_{\min})}\ln\left(\frac{T_{\max}^4 - T_{\mathrm{R}}^4}{T_{\min}^4 - T_{\mathrm{R}}}\right) \tag{14}$$

When the heat transfer coefficient is temperature independent as in case of conduction, previously described [10] then:

$$E = R\frac{T_{\max} T_{\min}}{T_{\max} - T_{\min}}\ln\left(\frac{\Delta T_{\max}}{\Delta T_{\min}}\right) \tag{15}$$

Results and discussion

The results obtained are presented in Figs 1–4. In all cases the products of the catalytic oxidation of methanol in oscillatory regime are CO_2 and H_2O [8].

The bifurcation diagram shown in Fig. 1 describes the influence of oxygen concentration upon the reaction rate observed via the difference in temperature ΔT. All other experimental parameters were kept constant. The stable state in Fig. 1 are represented by the full line where as the oscillations are given by vertical lines representing the amplitude of the oscillation.

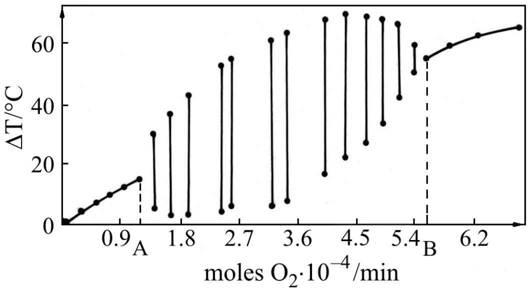

Fig. 1 Bifurcation diagram: temperature difference ΔT between the catalyst T and the temperature reactor T_R *vs.* oxygen content in the feed (T_R=80°C, 20 mg catalyst, methanol feed=$2.0\cdot10^{-5}$ mol min^{-1}); ● – values of the minimum and maximum temperature oscillations independently of the sense of increasing and decreasing the oxygen content in the feed

At low oxygen content only a stable steady state was observed. On increasing the feed of oxygen, in point A there is a transition to a stable oscillatory state. With the increase of oxygen feed the amplitude of oscillations increases, attains a maximum and then decreases to point B, where they disappear. This point B represents a new transition from a stable oscillatory state to a stable steady state.

A bifurcation diagram obtained by using the methanol content in the feed is presented in Fig. 2 using the same procedure as before.

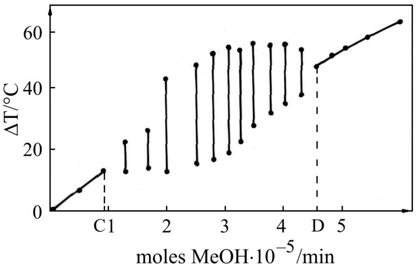

Fig. 2 Bifurcation diagram: temperature difference ΔT between the catalyst T and the temperature reactor T_R *vs.* methanol in the feed (T_R=80°C, 20 mg catalyst, oxygen feed=$4.7\cdot10^{-4}$ mol min^{-1}); ● – values of the minimum and maximum temperature oscillations independently of the sense of increasing and decreasing the oxygen content in the feed

Using the ΔT values obtained from Figs 1 and 2 the overall activation energy of the oscillatory behavior was determined by using Eqs (13), (14) and (15).

For the first bifurcation diagram the two linear dependencies of the overall activation energy upon the oxygen content were obtained for all the three heat loss laws, the intersecting point of the straight lines being situated around 4.0 mol O_2 (10^{-4} min^{-1}) (Fig. 3).

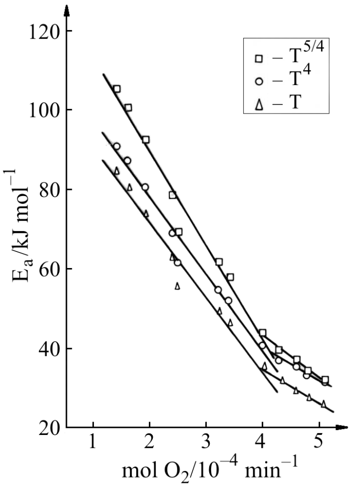

Fig. 3 Activation energy *E vs.* oxygen content in the feed

For the second bifurcation diagram also two linear dependencies occur for the overall activation energy upon the methanol concentration. The intersection point for all the straight lines is situated around 2.7 mol MeOH (10^{-5} min^{-1}) (Fig. 4).

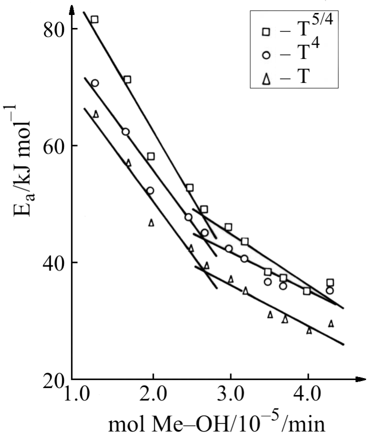

Fig. 4 Activation energy *E vs.* methanol content in the feed

The values of the minimum E_{TM} and maximum E_{TM} activation energies from Figs 3 and 4 together with the corresponding activation energy E_{Ti} in the intersection point are presented in Table 1.

Table 1 Values of the overall activation energy of methanol oxidation in oscillatory in kJ mol^{-1}

Changed in the feed	$E_{T^1_{\mathrm{m}}}$	$E_{T^1_{\mathrm{i}}}$	$E_{T^1_{\mathrm{M}}}$	$E_{T^4_{\mathrm{m}}}$	$E_{T^4_{\mathrm{i}}}$	$E_{T^4_{\mathrm{M}}}$	$E_{T^{3/4}_{\mathrm{m}}}$	$E_{T^{5/4}_{\mathrm{i}}}$	$E_{T^{5/4}_{\mathrm{M}}}$
Me-OH	28.4	38.4	65.2	34.0	43.8	70.8	32.5	47.9	81.5
O_2	25.7	35.5	84.2	31.5	41.4	90.8	32.1	43.7	105.3

E_{T^1}, E_{T^4} and $E_{T^{5/4}}$ are the overall activation energies in cases of a Newtonian, a radiation and a convection heat loss law respectively, the highest values being obtained in case of free convection loss.

The obtained values are within the range the activation energies for heterogeneous catalytic oxidation reactions [16].

During one period of oscillation, a large number of diffusion, adsorption, reaction and desorption steps will occur. More over, the catalyst itself may undergo changes like oxidation-reduction cycles or adsorbate-induced reconstruction [17]. Other authors have suggested that the slow formation and removal of subsurface oxygen in the system CO/Pd(110) single crystal is responsible for the oscillations [18, 19]. Using X-ray absorption spectroscopy (XAS) it was proved for the CO oxidation on Pd supported catalyst that the oxidation-reduction process is the driving force for producing oscillations [19]. The catalyst exhibits a decreasing activity with an increasing oxygen coverage and restoration of catalytic activity with the increase of CO content on the surface. This model represents a non-isothermal surface blocking/reactivating mechanism assuming a Langmuir-Hinshelwood mechanism for the reaction kinetics [21, 22]. This type of mechanism could be proposed for the system Me-OH/Pd supported catalyst too.

That is why the sequence of all these processes will be quite complex and this energy can not be attributed to a single rate-determining step [23]. Only the combination of all reaction steps yields an overall Arrhenius energy.

The existence of two intersecting straight lines for the activation energy could be an indication for the presence of two different pathways for the oscillatory oxidation of methanol on Pd-catalyst. These mechanisms could exist simultaneously on the surface and only the reactants concentration makes that one or another mechanism prevails.

For each reactant there exists a linear dependency between the overall activation energy and the surface coverage. This type of linear dependency suggests a non-uniform catalyst surface.

It must be also mentioned that our dynamic calorimeter was used only for solid-gas oscillatory systems. For liquid oscillatory reactions a mini-calorimeter [24] was recently developed.

Conclusions

A suitable method to investigate thermokinetic oscillations of methanol oxidation on Pd was developed. This method uses the minimum and maximum values of temperature oscillations.

In the first approximation one can use the conduction mechanism for the heat loss to the environment in order to calculate the overall activation energy of the thermokinetic oscillations.

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