Dedicated to Dr. Maria Zaharescu
*on the occasion of her 85th anniversary*

ACTIVATION ENERGY OF HETEROGENEOUS CATALYTIC OXIDATION OF METHANOL IN OSCILLATORY REGIME

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A new equation for the determination of activation energy of chemical oscillations was obtained in the reaction of methanol oxidation on a Pd catalyst. The maximum temperature, T_M, of oscillations depends on the arrangement of the same quantity of the catalyst in the reactor, with the other experimental conditions kept constant.

$$CH_3OH + O_2 \xleftarrow{\quad Pd \quad} Products$$
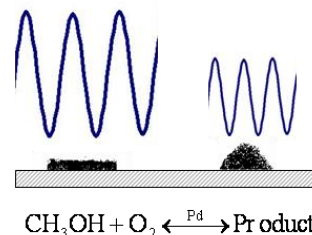
INTRODUCTION

Heterogeneous catalytic reactions are non-linear multi-level chemical reaction systems, far from thermodynamical equilibrium, which exhibit complex temporal behavior such as instabilities, oscillations, chemical waves, or chaos. Their behavior can be investigated at various levels for a heterogeneous catalyst system.[1]

There are some reasons for studying oscillatory catalytic reactions:[1-6]

1. Many surface reactions oscillate.
2. These reactions are still intriguing and poorly understood phenomena.
3. Oscillatory state of reactions is potentially dangerous in chemical plants.
4. For some oscillatory states, it is possible to obtain unstable operation regimes of the reactors.

The oscillatory behavior of methanol oxidation on a solid catalyst is normally observed at macroscopic scale as oscillations of the product amount at the outlet of a flow reaction, or as oscillations of a quantity that depends on the reaction conversion, i.e. as temperature oscillations.

In this paper, we study the influence of the catalyst bed packing in the reactor, during the oxidation of methanol on a Pd catalyst, and assess the activation energy of the oscillations observed.

RESULTS AND DISCUSSION

One period of a temperature oscillation is characterized by two points: a minimum point where the oscillations start and where the temperature is T_{min} and the maximum of the amplitude where the temperature is T_{max}[7,8] (Fig. 1).

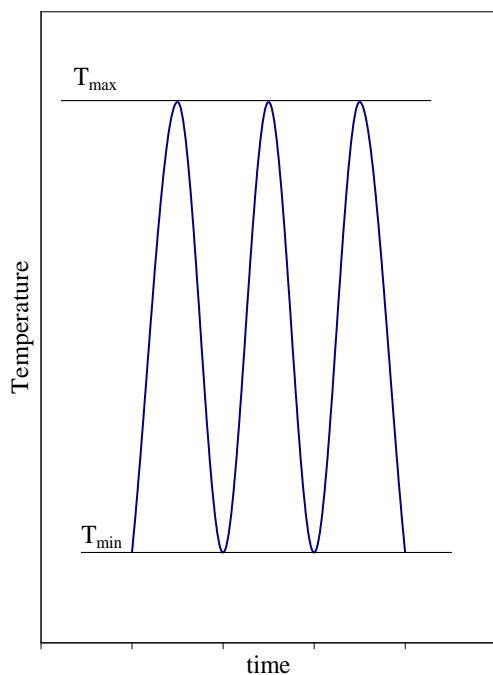* Corresponding author: ionescu@icf.ro

Fig. 1 – Time function of temperature oscillations.

The catalyst packing in the metallic sample holder is an important factor that determines the characteristics of the obtained oscillations and its effect is presented in Fig. 2. As can be observed in this figure, the catalyst powder distribution can induce thermal oscillations with alternatively high and small amplitudes. Such behavior was observed also in CO/Pd[9] and C_2H_5OH[10] systems.

During one period of oscillation, a high number of events occurs, such as diffusion, adsorption, reaction and desorption. Moreover, the catalyst itself may undergo changes like oxidation-reaction cycles or adsorbate-induced reconstruction.[12] It was suggested that the slow formation and removal of subsurface oxygen[5] is responsible for the oscillations. The sequence of all these processes is quite complex and the calculated activation energy value can not be attributed with certitude to a single rate-determining step and hence, the combination of all reaction steps would contribute to an overall Arrhenius-type energy.
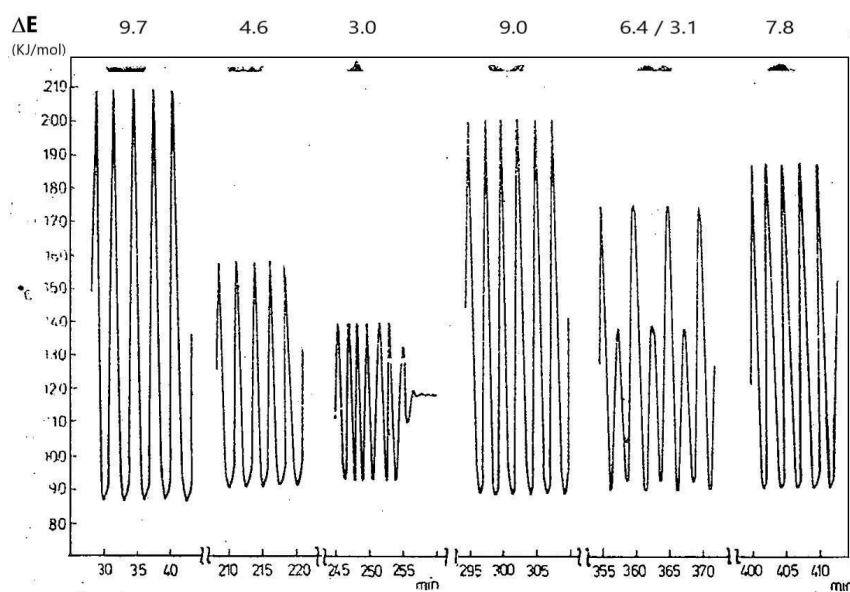

Fig. 2 – Thermal oscillations induced by different types of arrangement of the same catalyst sample on the holder in the reaction cell (adapted from Reference [11]).[11] Experimental conditions: weight of the catalyst sample: 18 mg; temperature of the reaction cell: 80°C; methanol content: 5%; oxygen flow rate: 5.0 ml/min.

In order to see what these oscillation energies represent, we assume now that, on a homogeneous surface, first-order desorption takes place in which re-adsorption occurs freely:

$$\theta_{Alc} + \theta_{O_2} = \theta_{CO_2} + \theta_{H_2O} = \theta \qquad (1)$$

where $\theta_{Alc}, \theta_{O_2}, \theta_{CO_2}$ and θ_{H_2O}, are the surface coverage degrees for alcohol, oxygen, carbon dioxide, and water, respectively.

To deduce the formula which will be used in this case, one starts from the known relationships:[13]

$$c = -\frac{V_s v_m \beta}{F} \cdot \frac{d\theta}{dT} \qquad (2)$$

and

$$c = v_m \frac{k_d}{k_a'} \cdot \frac{\theta}{1-\theta} \qquad (3)$$

where c is the concentration of a compound in the gas phase, V_s the volume of the catalyst bed, v_m – the amount of the same compound adsorbed per unit volume of the solid phase when $\theta=1$, F – the carrier gas flow rate, β – the linear heating rate, k_d the constant rate of desorption of products and k_a' the constant rate of adsorption of educts.

From equations (2) and (3) it follows that:

$$-\frac{d\theta}{dT} = \frac{F}{V_s\beta} \cdot \frac{k_d}{k_a'} \cdot \frac{\theta}{1-\theta} = \frac{F}{V_s\beta} \cdot \frac{\theta}{1-\theta} \cdot \frac{A_d \exp\left[-\left(\frac{E_{CO_2} + E_{H_2O}}{RT}\right)\right]}{A_a' \exp\left[-\left(\frac{E_{Alc} + E_{O_2}}{RT}\right)\right]}$$

and finally:

$$-\frac{d\theta}{dT} = \frac{F}{V_s\beta} \cdot \frac{\theta}{1-\theta} \cdot \frac{A_d}{A_a'} \cdot \exp\left[-\frac{(E_{CO_2} + E_{H_2O}) - (E_{Alc} + E_{O_2})}{RT}\right] \quad (4)$$

where A_d and A_a' are the entropic factors of desorption and adsorption respectively and E_i (where $i = CO_2$, H_2O, Alc, and O_2) – the respective activation energy.

At the maximum value of the peak: $\left(\frac{dc}{dT}\right)_{T=T_M} = 0$, where T_M is the temperature of an oscillation and is obtained from the difference between the maximum temperature of an oscillation T_{max} and the minimum temperature of it, T_{min}:

$$T_M = T_{max} - T_{min} \quad (5)$$

From Eqs. (3) and (4), considering θ_M – the surface coverage at T_{max}, it results:

$$\left(\frac{k_d}{k_a'}\right)_M = \frac{V_s\beta}{F} \cdot (1-\theta_M)^2 \frac{E_{CO_2} + E_{H_2O} - (E_{Alc} + E_{O_2})}{RT_M^2} \quad (6)$$

which can be written in the form:

$$2\ln T_M - \ln\beta = \frac{E_{CO_2} + E_{H_2O} - (E_{Alc} + E_{O_2})}{RT_M} +$$
$$+ \ln\left[\frac{(1-\theta_M)^2 \cdot (E_{CO_2} + E_{H_2O} - E_{Alc} - E_{O_2})V_s A_a'}{F \cdot R \cdot A_d}\right] \quad (7)$$

In the temperature programmed desorption, the temperature is usually continuously varied and the process is influenced by the manner in which it depends on temperature. In general, an analysis of such a process can be carried out only if the variation of the temperature with time is of a simple functional form.

In our case, this functional form is unknown because the temperature is increased by the reaction itself due to its exothermicity. That is why $\ln\beta$ is transferred into the right part of Eq. (7) *i.e.*:

$$2\ln T_M = \frac{\Delta E}{RT_M} + \ln\left[\frac{(1-\theta_M)^2 V_s\beta A_a'\Delta E}{F \cdot R \cdot A_d}\right] \quad (8)$$

where

$$\Delta E = E_{CO_2} + E_{H_2O} - (E_{Alc} + E_{O_2}) \quad (9)$$

The obtained ΔE values calculated with the relation (8) are presented in Fig. 2. Each of these oscillations shapes depend on the catalyst bed disposal in the reactor, the highest temperature being obtained with normal planar disposal and the smallest one with a catalyst agglomeration which reduces, probably the active surface. In case 5, the catalyst distribution in two parts that are not equal can be an explanation for the two different oscillations, obtained in the experimental conditions.

The different values of ΔE obtained in this non-isothermal process of oscillation demonstrate the importance of the catalyst's bed arrangement in the reactor. This could be an explanation for the different activation energies obtained in oscillatory processes with the same type of reactants.

The processes involved on the surface of the catalytically active Pd crystals are the adsorption of oxygen and alcohols, their reaction on the surface, and desorption of products (namely CO_2 and H_2O). Studies on the decomposition of methanol on Pd single crystals have shown that the chemistry of the reaction is complicated, consisting of methyl, methoxy, oxygen, CO, OH, and H intermediate species.[11] But the obtained products were CO_2 and H_2O.

The results can be qualitatively modeled as follows[14]: in the high-temperature range, the heated Pd clusters of the catalyst become progressively covered by oxygen which leads to slow oxidation of Pd.[3,15,16] At the same time the methanol is adsorbed on the surface and the temperature decreases reaching the low-temperature stage. At this point, the reaction reaches its critical conditions, and methanol is oxidized, the reaction being exothermal. Now, due to these surface reactions, the concentration of CH_3OH and O_2 diminishes and the oxidized Pd is reduced to Pd. The temperature increases during this stage and the high-temperature stage is reached again. A new oscillation can start. This model represents a non-isothermal blocking/reactivation mechanism assuming a Langmuir-Hinshelwood type reaction kinetic. The oxidation (blocking) – reduction (reactivating) process is assumed to be the driving force for the obtained oscillations in this case.

In modeling oscillations, two essential aspects are to be taken into consideration: on the microscopic level – to find the smaller unit, which is capable to

oscillate, and on the macroscopic level – to find the global synchronization mechanism which produces macroscopic variations of the reaction rate. The more general case is that of some non-linear processes which take place on a local scale but are not visible to observations, hence the seemingly trivial case of stationary rate is observed.

EXPERIMENTAL

The temperature difference between the catalyst sample and the gaseous mixture was measured in a dynamic calorimeter, the experimental installation being presented previously.[18] The catalyst used was $Pd/LiAl_5O_8$ (Bayer) with a granulation between 0.07 and 0.11 mm. The catalyst was placed on a silver plate connected to a thermocouple. The temperature difference (T) between the silver plate and the reaction gas is an indication of the combustion of methanol and was continuously registered. The oxygen flow rate was between 1.3 and 5.0 mL/min. The analysis of the products of the reaction was performed using a Carlo Erba gas chromatograph.

CONCLUSIONS

In conclusion, a new equation for determining the activation energy of chemical oscillations was obtained using only the maximum temperature obtained in the oscillatory reaction of methanol oxidation on a Pd catalyst. In the same experimental conditions, the maximum temperatures T_M of oscillations is different for different distributions of the same quantity of catalyst in the reaction cell (other experimental conditions of the reaction remain constant). The results have been discussed.

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