



Papers

*Dedicated to Professor Gheorghe Maria
on the occasion of his 70th anniversary*

OSCILLATORY BEHAVIOR OF METHANOL OXIDATION ON A SOLID CATALYST

Niculae I. IONESCU and Veronica BRATAN

“Ilie Murgulescu” Institute of Physical Chemistry, 202 Splaiul Independentei, 060021, Bucharest, Roumania

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Activation energies of chemical oscillations were determined in the reaction of methanol oxidation on a Pd catalyst. The maximum temperature oscillations depend on the concentration of the reactants. The obtained results are discussed.

$$2 \ln T_M = \frac{\Delta E}{RT_M}$$

INTRODUCTION

Heterogeneous catalytic reactions in solid-gas systems provide a variety of non-linear dynamic features because any heterogeneous catalytic reaction represents a non-equilibrium system. These chemical reactions exhibit complex temporal behavior such as instabilities, chemical waves, oscillations, or chaos.¹ The observed temporal behaviors depend not only upon the properties of local oscillations on each level but also upon the strength and nature of the coupling between them. The global oscillations observed require a coupling of a large number of oscillations in a microscopic state. These behaviors can be obtained and observed on various levels of heterogeneous catalytic systems.^{2–9}

The temperature oscillations observed during the oxidation of methanol on a Pd catalyst were

registered and considered like a non-isothermal process in which the necessary energy for oscillations was brought not from outside, but from inside, by the exothermic process of oxidation. Due to the exponential dependence of the rate constants on temperature, the nonisothermal conditions of the reaction can be expected to have a strong influence on the dynamic properties of those reaction systems and generate oscillatory behavior.

Any realistic system requires a large number of variables for its full description, but, due to a separation of time and length scales, only a few of these many degrees of freedom are really important for the dynamics of the system. Sometimes even only two variables are sufficient.

In this paper, the activation energy of the catalytic oxidation of methanol on a Pd catalyst is determined for the observed oscillations.

* Corresponding author: ionime@yahoo.com; ionescu@icf.ro

EXPERIMENTAL

The temperature difference between the catalyst sample and the gaseous mixture was measured in a dynamic calorimeter, the experimental installation being presented previously.^{10,11} The used catalyst was a Bayer on Pd/LiAl₅O₈ placed on a silver plate connected to a thermocouple, the combustion of methanol being continuously registered beginning with 25°C. The oxygen flow rate was between 1.3 and 15.0 mL/min. The analysis of products was performed using a Carlo Erba gas chromatograph.

RESULTS AND DISCUSSION

One period of a temperature oscillation has a minimum point where the oscillation starts, T_{\min} , which is, at the same time, the temperature of the ignition reaction, T_{ig} . The period of oscillation can be characterized by many events: the diffusion of the reactant of or in the catalyst, the adsorption on the surface, the reaction of reactants on or inside the surface, and desorption.

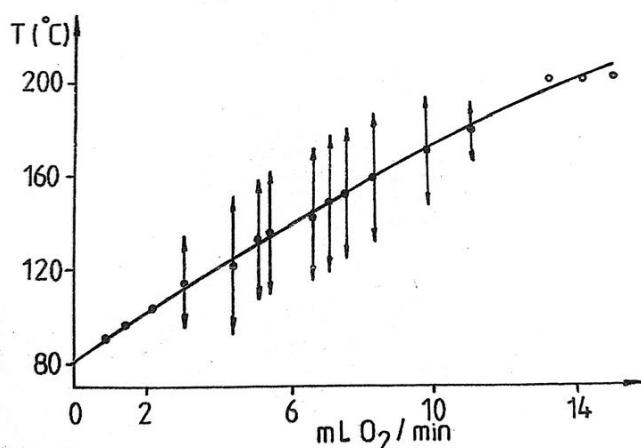


Fig. 1 – Temperature oscillations in catalyst bed (Pd/LiAl₅O₈) vs. oxygen content in the feed ($T_R = 80^\circ\text{C}$, 20 mg catalyst, methanol: 5%).¹²

In the case of the maximum temperature, the activation energy of oscillation was calculated with the formula (1):

$$2 \ln T_M = \frac{\Delta E}{RT_M} \quad (1)$$

where

$$\Delta E = E_{\text{CO}_2} + E_{\text{H}_2\text{O}} - (E_{\text{Alc}} + E_{\text{O}_2}) \quad (2)$$

and

$$T_M = T_{\max} - T_{\min} \quad (3)$$

and the values obtained are presented in Fig. 2. When the oscillations are finished, the activation energy decreases.

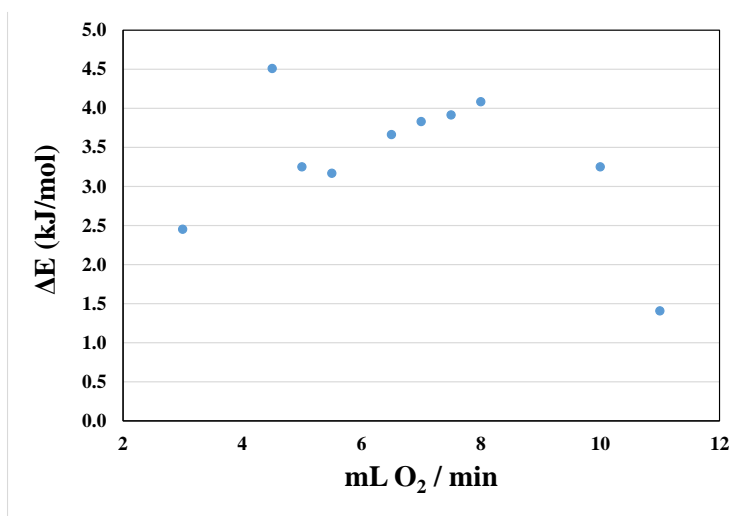


Fig. 2 – Values of activation energy obtained from equation (1).

The different values of ΔE obtained in this non-isothermal oscillation process demonstrate the importance of the reaction conditions. This could be an explanation for the different activation energies obtained in oscillatory reactions with the same type of reactants.

The processes involved on the surface of active Pd crystals are the adsorption of reactants, methanol and oxygen, their reaction on the surface and the desorption of products, in this case CO_2 and H_2O .

The catalyst can also be in oxidation reaction cycles or reconstruction induced by the adsorbates. Important also is the slow formation and removal of oxygen or reactants both being under or on the surface.^{13,14}

The methanol adsorption on Pd takes place in the manner known for C1-C4 alcohols on platinum metal.⁷ In the high-temperature range, the heated Pd clusters became covered by oxygen, leading to a slow Pd oxidation.^{13,14} At the same time methanol is adsorbed on the surface and the temperature decreases reaching its low-temperature stage. In these conditions, the reaction reaches its condition to start the methanol oxidation to CO_2 and H_2O . The surface concentration of methanol and oxygen diminishes and the oxidized Pd is reduced to Pd^0 . Because the temperature increases during this stage and the high-temperature stage is reached again. A new oscillation can start.^{11,12}

The model presented represents a non-isothermal blocking-reaction mechanism assuming a Langmuir-Hinshelwood reaction kinetic. The driving force of this reaction is a process of blocking (oxidation)-reactivating (reduction) of this catalytic reaction. Modification of the nature and local

distribution of the surface adsorbed species and surface defects produces the observed oscillation.

CONCLUSION

The activation energy values of the catalytic oxidation of methanol on Pd-supported oxides were determined in an oscillatory regime. While the concentration of methanol was kept constant, the temperature of oscillations depended on the concentration of oxygen.

REFERENCES

1. N.I. Ionescu and C. Hornoïu, in "Form and Patterns" eds. C. Vasilescu, M.-L. Flonta and I. Craciun, Roumanian Academy Printing House, **2015**, p.166
2. G. Ertl, *Adv. Catal.*, **1990**, *37*, 213
3. F. Schuth, B. E. Henry and L.D. Schmidt, *Adv. Catal.*, **1993**, *39*, 51
4. M.M. Slinko and N. I. Jaeger, *Studies in Surf. Sci. Catal.*, **1994**, vol.86
5. R. Imbihl, *Topics Catal.*, **2005**, *105*, 206
6. D. Luss and M. Sheintuch, *Catal. Today*, **2005**, *105*, 254
7. N. I. Ionescu, N.I. Jaeger, P.J. Plath, M.A. Lian and C. Hornoïu, *J. Therm. Anal. Cat.*, **2000**, *61*, 995
8. N. I. Ionescu, N.I. Jaeger, P.J. Plath and C. Hornoïu, *Rev. Roum. Chim.*, **2005**, *50*, 663
9. R. Imbihl, S. Ladas and G. Ertl, *Surf. Sci.*, **1989**, *1*,307
10. N. I. Ionescu, N.I. Jaeger, P.J. Plath and C. Hornoïu, *J. Therm. Anal. Cat.*, **2008**, *92*, 381
11. V. Bratan, and N.I. Ionescu, *Rev. Roum. Chim.*, **2023**, *68*, 135
12. N. I. Ionescu, M. Caldararu, C. Hornoïu and C. Munteanu, *Rev. Roum. Chim.*, **2007**, *52*, 765.
13. M.M. Slinko, N.I. Jaeger and P. Svensson, *J. Catal.*, **1989**, *118*, 349
14. Th. Ressler, M. Hagelstein, U. Hatje and W. Metz, *J. Phys. Chem. B*, **1997**, *101*, 6680

