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ACTIVATION ENERGY OF IGNITION FOR CATALYTIC OXIDATION OF ETHANOL IN OSCILLATORY REGIME

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Activation energies of ignition for the thermokinetic oscillations obtained during the heterogeneous catalytic oxidation of ethanol on Pd/Al_2O_3 in a dynamic calorimeter were obtained using the minimum values of the temperature oscillations. These activation energies of ignition are greater than the activation energies of the corresponding oscillations. The obtained results are discussed by assuming a PdO_x redox cycle.

Keywords: *activation energy of ignition, heat loss, thermokinetic oscillations*

Introduction

The ignition – extinction of catalytic reactions is an important problem for the understanding of catalytic surface reactions such as the oxidations of hydrocarbons or other substances [1–8]. Ethanol can be catalytically oxidized either in steady state or in an oscillatory regime [9–12].

Oscillations in heterogeneous catalytic systems 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 on the conversion i.e. as temperature oscillations.

The highly exothermic catalytic oxidation of ethanol on Pd/Al_2O_3 was monitored by recording the catalyst temperature T *vs*. the temperature of the reactor T_R.$\Delta T=T-T_R$ corresponds either to a steady state rate of reaction or to the dynamic behavior of the system, e.g. in the case of oscillations [9–12].

In this paper, we try to obtain more information related to the ignition of the observed oscillations by focusing our attention to the minimum values of the temperature oscillations that can be reliably determined. With these values it was possible to obtain the activation energy of ignition for the oxidation of ethanol in the oscillatory regime. This approach will be demonstrated by analyzing temperature oscillations during the heterogeneously catalyzed oxidation of ethanol on a Pd/Al_2O_3 catalyst.

Experimental

The reactor was a continuous-flow calorimeter made of glass improved after a model which was developed by Kral [13]. The catalyst, an amorphous 5 mass% $Pd-Al_2O_3$ (Fluka) with a grain size of 80–100 μm, was placed on a silver plate of 8 mm diameter connected to a NiCr–Ni thermocouple. The difference in temperature (ΔT) between the silver plate and the reaction gas was a measure for the reaction rate of the complete combustion of ethanol and was continuously registered.

Ethanol was oxidized with a synthetic dried air (Messer–Grieshein) and the stream was regulated by thermal mass flow controllers. The total gas flow used was 43.2 mL min^{-1}.

The reaction products were analyzed by gas chromatography (Carlo Erba Fractovap 2350) and by quadrupole mass spectrometry (MS Leybold – Heraeus, Quadruvac 200) [9, 10].

Problems concerning the role of injection velocity on the spatial localization of a mixture, including the modeling of this effect were recently discussed [14, 15].

It must be mentioned that our dynamic calorimeter was used only far solid-gas oscillatory systems. For liquid oscillatory reactions a mini-calorimeter was developed [16].

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} (Fig. 1) [11, 17].

As pointed out [12] in temperature oscillations T_{min} plays an important role because at this temperature

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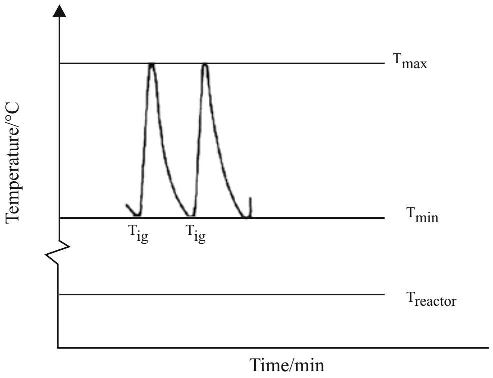

Fig. 1 Time function of temperature oscillations

the chemical reaction attains the critical conditions for an oscillation to start.

In order to obtain the activation energy E of ignition of the oscillatory reaction of ethanol oxidation on Pd/Al_2O_3 catalyst we have used a formula given by Hiam *et al.* [18]:

$$\frac{E}{RT_{ig}}=\ln\left[\frac{n}{(T_{ig}-T_0)^2}\right]+\ln\left(\frac{QART_0^2}{E\alpha}\right) \qquad (1)$$

where, T_{ig} is the temperature of ignition according to Fig. 1, $T_{ig}=T_{min}$, $T_0=T_R$ and n=reaction order in Et–OH or O_2, Q=reaction enthalpy, α=heat transfer coefficient, A=pre-exponential coefficient.

Due to the experimental conditions in which in the oxidation reaction either the concentration of ethanol (Et–OH) or of oxygen has been changed, the other component of the feed remaining constant [10–12] n can be taken as 1.

Thus a plot $\ln\left[\frac{1}{(T_{ig}-T_R)^2}\right]$ *vs.* $1/T_{ig}$ should lead to a straight line of slope E/R. The ignition temperature of oscillations was obtained from the bifurcation diagrams [11, 12]. A bifurcation diagram records qualitatively changes in the dynamic behavior of the system depending upon the experimental parameters which could be the bifurcation parameters. The bifurcation diagram represents the transformation of a steady state into an oscillatory one.

The bifurcation diagrams were obtained in two separate experimental conditions in which either the influence of oxygen or the ethanol concentrations upon the reaction rate were observed via the difference in temperature ΔT. The minimum temperature where oscillation starts T_{ig} and the maximum temperature attain by the oscillation T_{max} were determined independently of the sense of increasing or decreasing the oxygen or the ethanol contents in the feed, the other reactant, ethanol or oxygen concentrations respectively, remaining constant. The results of these measurements were analyzed graphically in Figs 2 and 3. From the slope of these lines the activation energy for the catalytic ignition of the oscillations was computed.

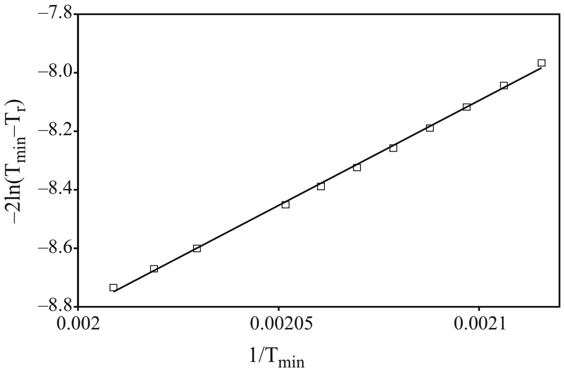

Fig. 2 Determination of ignition activation energy in case of constant oxygen concentration. Experimental conditions: T_R=146°C, 27.8 mg catalyst, 14.7 vol% oxygen, between 3 and 6 vol% ethanol

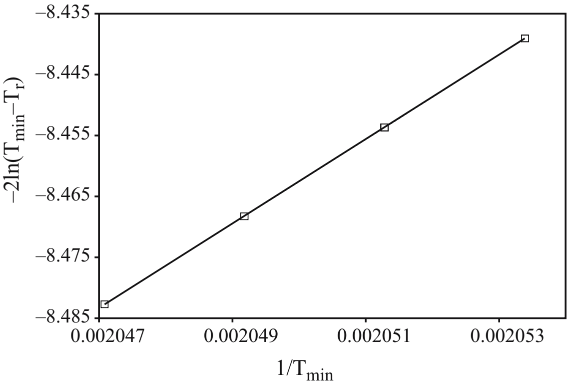

Fig. 3 Determination of ignition activation energy in case of constant ethanol concentration: T_R=146°C, 27.6 mg catalyst, 4.01 vol% ethanol, between 9 and 18 vol% oxygen. Each point represents two very narrow points

In case when the ethanol concentration was changed at a constant value of the oxygen concentration the activation energy was 59.6±1.2 kJ mol^{-1} (Fig. 2). When the oxygen concentration was changed at a constant concentration of ethanol, the activation energy was 57.6±1.4 kJ mol^{-1}(Fig. 3). These very close values suggest that the necessary activation energy of ignition for a temperature oscillation to start is the same, independent of the changing parameter ethanol or oxygen.

The results could be qualitatively explained by assuming a redox cycle as proposed in [19, 20]. In the high temperature range the hot surface of the Pd clusters of the catalyst becomes progressively oxidized to PdO_x with $0<x<1$. Due to oxidation of the metal surface, the reactivity drops, the temperature decreases and reaches the lowest point T_{min}. On the oxidized surface the oxygen sticking coefficient should be very small. At this point the oxide surface will be reduced by the alcohol until enough Pd empty sites become available and the dissociative adsorption of alcohol as the first step of the reaction becomes possible. The total oxidation of ethanol to CO_2 and H_2O [12, 17] can ignite, again. As a result of surface reactions the concentration of ethanol and oxygen diminishes on the surface. The temperature increases during this stage and the high temperature point T_{max} is reached again. 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 [21–24].

The obtained values are approximately two times greater than the activation energies of oscillations, which were around 35 kJ mol^{-1} in both cases and were determined using a nonisothermal kinetics [12, 17].

The ethanol adsorption on Pd takes place in the manner known for the C_1–C_4 alcohols on platinum metals [25]. The ethanol molecule contains two carbon atoms and can be split at several bonds, depending on the type of interaction with the catalyst and the reaction conditions. On palladium the first step of reaction is a dissociative adsorption [25]. Through several consecutive reactions of dehydrogenation and oxidation, with CO and H_2 as intermediates, as in case of methanol [26–29] one obtains the final products CO_2 and H_2O [19]. This happened in case of oscillations too, where only CO_2 and H_2O are determined [12, 17]. The determined energy of ignition is needed for obtaining the critical concentration of reactants and for the ignition of two oxidation reactions, namely the oxidations of CO and of H_2 with as long as free sites for the dissociative adsorption of oxygen are available. They disappear due to the formation of PdOx [30] in the redox cycle.

These activation energies of ignition cannot be attributed to a single rate-determining step, because the processes of obtaining the reactants will be quite complex. Only the combination of all reaction steps yields an overall activation energy of ignition for a lumped system that we are not able to model at the present time.

This fact is an indication that the beginning of an oscillation needs more energy to start than for it to develop, the ignition of the surface reaction in the oscillatory regime being an essential requirement in these catalytic processes.

Our results indicate that in the case of thermokinetic oscillations there are two types of activation energies one that is necessary to begin the processes and another that is necessary to develop the oscillation.

Conclusions

The overall activation energy of ignition for the catalytic oxidation of ethanol on a palladium supported catalyst in oscillatory regime was determined using the minimum values of temperature oscillations. The obtained values are greater than the overall activation energies of the corresponding thermokinetic oscillations. These results could be an indication that there are two types of activation energies in case of thermokinetic oscillations: one that is necessary to start the process of dissociative adsorption and another to develop the oscillation.

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