

HEAT AND MASS TRANSFER
IN HETEROGENEOUS CATALYSIS. XXIII.*

STUDY OF EFFECTS
OF HEAT AND MASS TRANSFER
BETWEEN THE EXTERNAL CATALYST PARTICLE SURFACE
AND THE BULK OF THE REACTION MIXTURE
ON DYNAMIC BEHAVIOUR OF CATALYST PARTICLES
FOR REACTION OF HYDROGEN WITH OXYGEN

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If the course of an exothermic catalytic reaction is affected by imperfect heat and mass transfer between the external surface of catalyst particles and the bulk of the reaction mixture (further called external heat and mass transfer), the catalyst particle in a steady state has a higher temperature as compared with the flowing reaction mixture. As this temperature difference is dependent on partial pressure of the reactant, at partial pressure change of the reactant the temperature of the catalyst particles must change to reach a new steady state. Due to the thermal capacity of catalyst particles, their temperature is not changing immediately but in a period of time. In one paper of this series¹ the effect of external heat and mass transfer on the course of steadying of catalyst particles regime by use of a mathematical model was studied. It was determined that the time of steadying of the regime should profoundly depend for strongly exothermic reactions on reaction conditions *e.g.* on partial pressure of the reactant. Greater difference in times of steadying at different partial pressures of the reactant may be expected especially when in a certain region of partial pressures of reactant two steady states may exist for one value of partial pressure. The aim of this paper is to verify experimentally the conclusions made on basis of the mathematical model.

EXPERIMENTAL

As a model reaction was chosen the reaction of hydrogen with oxygen. The measurement was made in a flow reactor of an inside diameter 20 mm in which one pellet of catalyst — platinum on alumina (0.5 weight % of Pt) was hanged. Dimensions were 7.2 mm (diameter) × 7.1 mm (height). The reacting mixture contained 0—3.9 vol% of hydrogen in air and the reaction conditions were chosen so that the conversion of hydrogen for one pass of the reaction mixture through the reactor was less than 0.25. The apparatus, the analytical methods, temperature measurement in the catalyst pellet, and the procedure for calculation of the rate constant and of the heat and mass transfer coefficients, are described in the preceding paper of this series².

All measurements were made at temperature 10°C of the flowing reaction mixture and with the flow rate of the reaction mixture through the reactor 200 l/h (at 20°C). For each experiment the catalyst pellet was brought to a steady state at a zero partial pressure of hydrogen or at partial pressure of hydrogen 0.035 atm. At the beginning of the experiment, the partial pressure of hydrogen was changed by a step change to the requested value and the way of steadying of the pellet regime by measuring of temperature at its centre was followed. In a steady state,

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also the reaction rate was determined from the composition of the reaction mixture leaving the reactor. The result of this measurements were the dependence of temperature at the catalyst pellet centre on the time of experiment and the reaction rate and temperature at the catalyst pellet centre in the steady state on different partial pressures of hydrogen in bulk of the reaction mixture.

RESULTS AND DISCUSSION

The dynamic behaviour of the catalyst pellet was studied at conditions when the effect of external heat and mass transfer is so profound that a region of partial pressure of hydrogen exists, in which at one value of partial pressure two stable steady states may exist. This region will be further called the hysteresis region. The reasons for existence of two stable steady states and of hysteresis in dependence of reaction rate on partial pressure of the reactant was discussed in the preceding paper of this series¹. Due to the existence of the hysteresis region, is the dependence of reaction rate in a steady state on partial pressure of hydrogen discontinuous and consists of two branches which will be further denoted as kinetic and diffusion branches. On the kinetic branch are situated the steady states with a lower reaction rate, on the diffusion branch are situated the steady

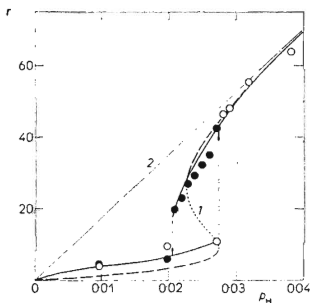


FIG. 1

Dependence of Reaction Rate r (mol/kg_{cat} h) on Partial Pressure of Hydrogen p_H (atm) at 10°C

Empty points denote values measured at a gradual increase of partial pressure of hydrogen, full points at its decrease. 1 Calculated dependence for $E = 11.5$ kcal/mol, $r_{omn}(10^\circ\text{C}) = 4.075$ mol/kg_{cat} h, $k_g = 2.77$ kg · mol/m² atm h, $k_b = 41.7$ kcal/m² °C h, $p_{Him} = 0.038$ atm, 2 curve denoting the region of external heat and mass transfer.

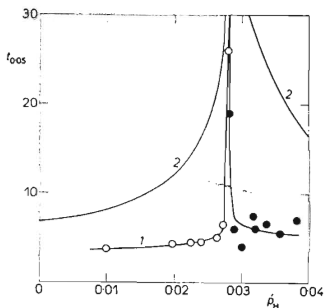


FIG. 2

Dependence of Steadying Temperature of the Catalyst Pellet $t_{0-0.5}$ (min) on Partial Pressure of Hydrogen p_H (atm) at 10°C for the Case, when at the Beginning of the Experiment the Partial Pressure of Hydrogen Was Null

1 Measured dependence, 2 calculated dependence for the case given in Fig. 1 (curve 1). Empty points denote values obtained by measurements on the kinetic branch of the reaction rate dependence on partial pressure of hydrogen, full points obtained on the diffusion branch.

states with a higher reaction rate. The measured dependence of the reaction rate in steady state on partial pressure of hydrogen is presented in Fig. 1.

In the hysteresis region the catalyst pellet may act in two steady states. That one in which the regime will become steady depends on temperature of the pellet at the beginning of the experiment. To get the way of steadying into steady states on the kinetic as well as on the diffusion branch the course of steadying was studied for two different initial states of the pellet. In first set of experiments at the beginning of the experiment, the pellet temperature was equal to the temperature for the flowing gas *i.e.* the pellet was before the step change of partial pressure of hydrogen in steady state at the zero partial pressure. The regime of pellet in the hysteresis region became steady on the kinetic branch. In the second set of experiments the pellet was heated before each experiment to a higher temperature by reaching a steady state at the partial pressure of hydrogen 0.035 atm and then the partial pressure was decreased to the required value. The pellet regime in the hysteresis region was steadying on the diffusion branch.

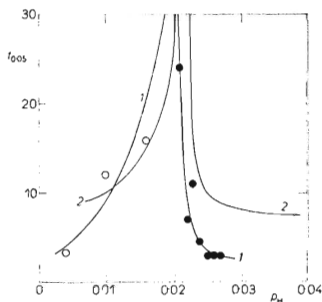


FIG. 3

Dependence of Time of Steadying of Temperature of Catalyst Pellets $t_{0.05}$ (min) on Partial Pressure of Hydrogen p_H (atm) at 10°C for the Case when at the Beginning of the Experiment the Partial Pressure of Hydrogen was 0.035 atm

1 Measured dependence, 2 calculated dependence for the case given in Fig. 1 (the calculation for curve 1 was made for value p_H (atm) at the beginning of the experiment 0.051). Other symbols used are the same as in Fig. 2.

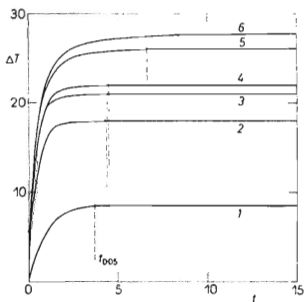


FIG. 4

Experimental Dependence of Temperature Difference between the Catalyst Pellet Centre and the Flowing Reaction Mixture ΔT ($^\circ\text{C}$) on Time of Experiment t (min) at 10°C . At the beginning of the Experiment the Partial Pressure of Hydrogen Was Null

$t_{0.05}$ Time of temperature steadying in which the difference between the instant catalyst pellet temperature and temperature in steady state equals 5% of the difference between the initial pellet temperature and temperature in steady state. 1 $p_H = 0.0098$ atm, 2 $p_H = 0.0195$ atm, 3 $p_H = 0.0225$ atm, 4 $p_H = 0.0237$ atm, 5 $p_H = 0.0269$ atm, 6 $p_H = 0.0275$ atm.

For a quantitative comparison of times of steadying at different partial pressures of hydrogen, as the time of steadying $t_{0.05}$ was chosen the time of experiment in which the difference between the instant pellet temperature and the temperature in steady state equals 5% of the difference between the initial pellet temperature and temperature in steady state.

For time of steadying defined in this way, if $t = t_{0.05}$ holds

$$(T_s - T_u)/(T_{in} - T_u) = 0.05. \quad (1)$$

Experimentally determined dependence of time of steadying on partial pressure of hydrogen is plotted in Fig. 2 and 3. From comparison of this dependence with the dependence of the reaction rate in steady state on partial pressure of hydrogen (Fig. 1) follows that, closely to the hysteresis region, the steadying of the pellet regime is extremely slow. This result is in agreement with the conclusions made from the study of dynamic behaviour of the catalyst pellet by use of the mathematic model of the pellet¹.

Further on, only the case is discussed where at the beginning of the experiment the temperature of the pellet equals the temperature of the flowing gas. The discussion of the case when the pellet at the beginning of the experiment has a higher temperature than in steady state is completely analogical. If at the beginning of the experiment the pellet temperature equals the temperature of the flowing gas it will be possible to reach all steady states on the kinetic branch and steady states on the diffusion branch beyond the hysteresis region. For steadying in a state on the kinetic branch, the time of steadying increases with the increase of the partial pressure of hydrogen. The highest but final values on the kinetic branch are obtained for time of steadying at highest values of partial pressure of hydrogen in the hysteresis region. Examples of measured dependence of temperatures of catalyst pellets on times of steadying of the experiments are given in Fig. 4. For steadying in states on the diffusion branch, the states on the diffusion branch inside the hysteresis region cannot be reached. For states on this part of the curve are the steadying times infinitely large. Above the hysteresis region, the steadying time decreases with increasing partial pressure of hydrogen from infinity to values comparable with time of steadying on the kinetic branch. In cases, when the partial pressure of hydrogen is close to the hysteresis region and the pellet is passing through states close to the steady states on the kinetic branch, is in the dependence of the pellet temperature on time of the experiment a profound region of constant tempera-

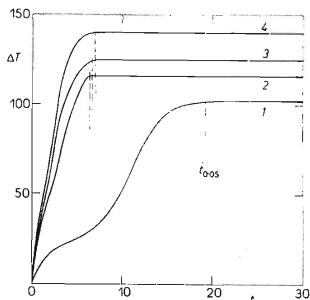


FIG. 5

Experimental Dependence of Temperature Difference between the Catalyst Pellet Centre and the Flowing Reaction Mixture ΔT ($^{\circ}\text{C}$) on Time of Experiment t (min) at 10°C . At the Beginning of the Experiment the Partial Pressure of Hydrogen Was Null

Symbols used are the same as in Fig. 4.
 1 $p_{\text{H}} = 0.02$ atm, 2 $p_{\text{H}} = 0.0315$, 3 $p_{\text{H}} = 0.0335$ atm, 4 $p_{\text{H}} = 0.0379$ atm.

ture (the dependence has an inflex point). Examples of dependences of temperature on time of experiment are given in Fig. 5.

In the preceding paper², the possibility was discussed of application of the mathematical model of the catalyst pellet affected by the external heat and mass transfer on steady state of the pellet. It was found that application of the mathematical model gives only qualitative agreement with experimental values if the rate constant and activation energies for the considered reaction are used (k (0°C) = 404 ± 80 mol/kg_{cat} h atm, $E = 5.1 \pm 1$ kcal/mol). A better agreement may be got by using profoundly higher values of activation energy of the reaction. To a similar conclusion leads also the application of the mathematic model to the dynamic behaviour of the catalyst pellet. Comparison of examples of calculated and measured dependences of the reaction rate and of the time of steadying on partial pressure of hydrogen are in Figs 2 and 3. From literature, the specific heat of catalysts is in the range of 0.1–0.2 kcal/kg_{cat} °C. For calculation the value 0.1 was considered.

Disagreement of the mathematical model with the experimental values may be the consequence of unfulfillment of some of assumptions used for derivation of the model. Let us assume further that probably simultaneously applies some other effect which was not included in the simple model *e.g.* the catalyst activity and thus the reaction rate is affected by chemisorption of water on the catalyst surface. In more detail, the reasons of disagreement of calculated and measured dependences are discussed in the preceding paper of this series².

LIST OF SYMBOLS

| | |
|------------|--|
| E | activation energy of the reaction |
| k_g | mass transfer coefficient |
| k_h | heat transfer coefficient |
| k | rate constant |
| p_{H_2} | partial pressure of hydrogen in bulk of the reaction mixture |
| p_{H_2m} | standard partial pressure of hydrogen in bulk of the reaction mixture |
| r | reaction rate |
| r_{omn} | reaction rate related to the standard temperature and partial pressure of hydrogen in bulk of the reaction mixture at conditions when the effect of external heat and mass transfer is eliminated |
| t | time of experiment |
| $t_{0.05}$ | time of steadying in which the difference between the instant catalyst pellet temperature and temperature in steady state equals 5% of the difference between the initial pellet temperature and temperature in steady state |
| T | temperature of bulk of the reaction mixture |
| T_{in} | initial temperature of the catalyst pellet surface |
| T_s | temperature of the catalyst pellet surface |
| T_u | temperature of the catalyst pellet surface in steady state |

REFERENCES

1. Horák J., Jiráček F.: This Journal, in press.
2. Horák J., Jiráček F.: This Journal, in press.

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