
HEAT AND MASS TRANSFER IN HETEROGENEOUS CATALYSIS. XXXII.***EXPERIMENTAL STUDY OF DYNAMIC BEHAVIOUR OF THE CATALYTIC TUBULAR FLOW REACTOR**

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The effect of heat and mass transfer at the external surface of the catalyst particle was studied experimentally on dynamic behaviour of the tubular flow reactor at the constant temperature of the bulk of the reaction mixture. The reaction of hydrogen with oxygen on the platinum catalyst is used as a model reaction. The measurements were made with a single catalyst pellet situated in a batch reactor with a tubular recycle of the reaction mixture. The apparatus enabled modelling of dynamic behaviour of the tubular reactor at a step composition change of the reaction mixture at the inlet into the reactor through a cascade of mixed reactors with a large number of reactors. It was confirmed in agreement with the conclusions of the theoretical study of the mathematical model of the operation that two stable steady states of the catalyst particle exist in a certain range of hydrogen concentrations in the mixture at one concentration.

The results of a theoretical study of the effect of heat and mass transfer at the external surface of the catalyst particle (further on denoted as the external heat and mass transfer) on dynamic behaviour of the isothermal flow reactor with plug flow are verified experimentally. This problem has not yet been studied in technical literature.

From a theoretical study¹ follows, that due to the effect of external heat and mass transfer some catalyst particles in the tubular reactor can operate in two stable steady states. In the reactor then exists a part of the catalyst bed in which the particles operate in one of the two possible steady states in dependence on the initial particle temperature and concentration of the reactant at the reactor inlet. As a model reaction for verification of the results of the theoretical study was used the reaction of hydrogen with oxygen on the platinum catalyst. In one of the previous papers² has been experimentally proved, that for a given reaction in a certain region of reaction conditions two stable steady states of the catalyst particle exist at one hydrogen concentration in the mixture.

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EXPERIMENTAL

For the model reaction was used the reaction of hydrogen with oxygen. The catalyst was platinum on alumina (platinum content 0.3 weight %). The measurements were performed in a batch reactor (I.D. 10 mm) with a tubular recycle of the reaction mixture ($400 \text{ cm}^3/\text{s}$) on a single catalyst pellet (diameter 4.85 mm) at barometric pressure and temperatures 10 and 20°C in the range of hydrogen concentrations 0 to 4 vol.%. The recycle of the reaction mixture was arranged by a polyethylene hose of 10 mm I.D. 825 mm long, separated into two parts. Before the measurement both parts were filled with mixtures of different hydrogen concentration in the air, the apparatus was closed and the circulating pump was switched on. The use of a long tubular recycle enabled preservation of changes of hydrogen concentration which were taking place at steadying of the regime of the catalyst particle. Then the modelling of the dynamic behaviour of the tubular reactor at a step change of hydrogen concentration in the inlet mixture into the reactor could be modelled by the behaviour of a cascade of mixed reactors with a large number of reactors. The arrangement of the apparatus is schematically presented in Fig. 1. The hydrogen concentration in the reaction mixture at the reactor outlet was measured as well as the temperature difference between the catalyst centre of the particle and the bulk of the reaction mixture (this temperature difference was used as an approximation of the actual temperature difference between the external particle surface and the bulk of the reaction mixture). The purification and feeding of hydrogen and air, the analytical method, and the temperature measurement of the catalyst particle are given in detail in the preceding papers of this series^{2,3}.

RESULTS AND DISCUSSION

The tubular reactor with plug flow may be considered to be a cascade of mixed flow reactors with infinite number of reactors. The batch reactor with the tubular recycle of the reaction mixture made possible the simulation of the behaviour by a cascade of mixed flow reactors. One passage of the mixture over the catalyst particle thus corresponded to the operation which took place in one reactor of the cascade. On the used experimental apparatus could be thus verified the conclusions of the study of dynamic behaviour of the tubular flow reactor which were obtained by the mathematical model. When one part of the pipe of the reactor recycle was filled by the reaction mixture of the initial hydrogen concentration c_{H_1} and the second by the mixture of initial hydrogen concentration c_{H_2} , it was possible to obtain by evaluation of the experimental data the concentration changes and the temperatures of the catalyst particles along the tubular reactor at the transition from the steady state at the concentration c_{H_1} to the steady state at the concentration c_{H_2} . The main attention was paid to the case when c_{H_1} equals to zero which is analogical to the beginning of the operation of the tubular flow reactor. The measurements resulted in dependence of the hydrogen concentration in the mixture and the catalyst particles temperatures on the time of experiment. Examples of measured dependences are given in Figs 2 and 3. These dependences describe directly the temperature changes of the catalyst particles and the hydrogen concentration in the reaction mixture in the given reactor of the cascade if the initial hydrogen concentration in the mixture is changed. From these dependences were determined the dependences of hydrogen

concentrations in the mixture and the temperature of the catalyst particles on time of the experiment for the given reactor of the cascade in such a way that the moment the step concentration change is passing over the particle was considered as the moment of beginning of a dynamic operation in the given reactor of the cascade (Figs 4 and 5). From the time dependences were then determined the trajectories of the variation of regimes of individual reactors of the cascade in the phase plane particle temperature—hydrogen concentration in the reaction mixture and the longitudinal profiles of hydrogen concentration and particle temperature in the tubular reactor for various times from the beginning of the dynamic operation.

Trajectories of Motion of the Reactor Regime

For description of dynamic behaviour of the reactor it is suitable to determine the trajectories of motion of the regime of the catalyst particle in the phase plane particle temperature, hydrogen concentration in the reaction mixture. These trajectories are not supplying information concerning the rate of operation but they give ideas concerning the path the particle regime comes from one state into the other. In this phase plane is situated the curve of stable steady states of catalyst particles². It de-

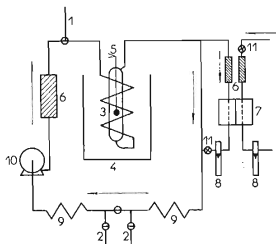


FIG. 1

Experimental Station

1 Inlet of reaction mixture, 2 outlet, 3 reactor, 4 thermostat, 5 thermocouple, 6 drier, 7 conductivity cell, 8 flowmeter, 9 recycle pipe, 10 circulating pump, 11 control valve.

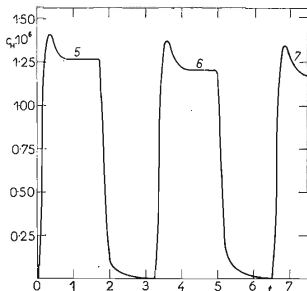


FIG. 2

Example of Experimental Dependence of Hydrogen Concentration in the Reaction Mixture at the outlet from the Reactor (mol/cm^3) on Time of Experiment (min) for Temperature 20°C and Initial Hydrogen Concentration in Mixture $1.59 \cdot 10^{-6} \text{ mol}/\text{cm}^3$

5 Fifth passage of reaction mixture through the reactor, 6 sixth passage of reaction mixture through the reactor, etc.

termines the temperature of the catalyst particle kept in a mixture of constant concentration. The steady states of catalyst particles must be situated on this curve. At the studied conditions the curve of steady states has two branches: the kinetic and the diffusion. As these branches are mutually separated, the particle regime must transfer from one branch to the other by a step change. On the kinetic branch the temperature of the particle is low, the hydrogen concentration on the surface is high; on the contrary on the diffusion branch the particle temperature is high and the hydrogen concentration on the surface is low. The curve of steady states of the catalyst particles (in Fig. 6 is denoted by a dashed line) was determined from the results of measurements in the case the whole reactor recycle was filled by the reaction mixture of one composition. At these conditions the regime of the particles is situated in a pseudostationary state close to the curve of steady states.

The existence of two steady states of the catalyst particles in a cascade enables, at one composition of the reaction mixture at the reactor inlet, steadying of several steady states. A certain number of reactors of the cascade can then operate in the first or in the second stable steady state. In general, the selection of the given steady state may be quite arbitrary and the number of states of the cascade is given by all combinations of individual possibilities. For an actual dynamic operation it is possible to expect the regime in individual reactors to steady in such a way that in the region of existence of two states of the particle are formed two sections of the cascade.

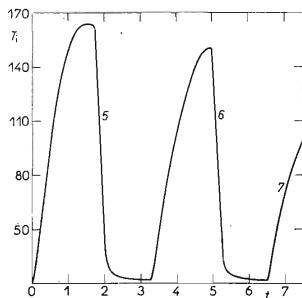


FIG. 3

Example of Experimental Dependence of Temperature of Catalyst Particle ($^{\circ}\text{C}$) on Time of Experiment (min) for the Case Given in Fig. 2

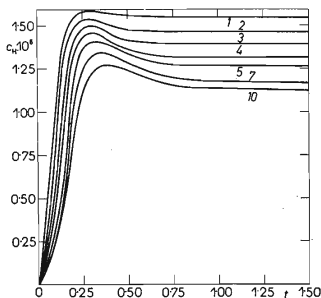


FIG. 4

Example of Steadying of Hydrogen Concentration in Reactor (mol/cm^3) at Individual Passages of Reaction Mixture Through the Reactor for the Case Given in Fig. 2

The numbers denote passages of reaction mixture through the reactor.

In one section all the reactors will operate in the kinetic regime in the second section in the diffusive regime. An example of distribution of steady states between these sections is given in Fig. 6. The way the reactors of the cascade are distributed between these sections depends in general on the initial temperature of the catalyst particle and on the initial hydrogen concentration in all reactors of the cascade.

Thermal capacity of the catalyst on the basis of an analysis in the given unit (this conclusion is valid for tubular reactors as well) is much greater than the mass of the reaction mixture. The dynamic operations are at negligible mass of the reactor determined by the dynamics of temperature variation of the catalyst particles with the hydrogen concentration in the bulk of the reaction mixture in pseudostationary state¹. The initial temperature of the particle (*i.e.* the temperature before the change in hydrogen concentration in the mixture) is decisive for the state the particle will steady in. This is affected simultaneously by hydrogen concentration in the mixture after the made concentration change.

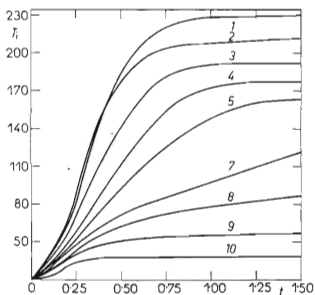


FIG. 5

Example of Temperature Steadying of Catalyst Particle ($^{\circ}\text{C}$) at Individual Passages of Reaction Mixture Through the Reactor for the Case Given in Fig. 2

Symbols used are the same as those used in Fig. 4.

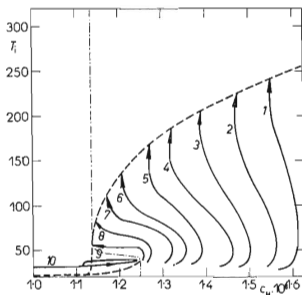


FIG. 6

Dependence of Temperature of Catalyst Particles ($^{\circ}\text{C}$) on Hydrogen Concentration in the Bulk of Reaction Mixture (mol/cm^3) for 20°C and Initial Hydrogen Concentration in Mixture $1.59 \cdot 10^{-6} \text{ mol}/\text{cm}^3$

Solid line represents trajectories of steadying of particle temperatures at individual passages of reaction mixture through the reactor, dashed line the dependence of stable steady particle states, dashed and dotted the separatrix. The numbers denote passages of reaction mixture through the reactor.

The motion of individual reactors of the cascade on the phase plane is rather complicated as the operation in the given reactor depends on the dependence of the inlet hydrogen concentration in this reactor on time and the inlet concentration is the result of dynamic operations in all preceding reactors. The motion of the regime can be considered the result of two operations *i.e.* of the temperature changes of the particle in the given reactor and composition changes at the inlet into this reactor. If the inlet concentration into the reactor is constant, as with the first reactor the behaviour is simple. The motion of the regime is affected only by the temperature changes of the catalyst particles. Therefore the regime of the particle moves along the curve close to the straight line $c_H = \text{const}$. Whether it moves toward the state on the kinetic or diffusion branch depends on the position in respect to the separatrix. The separatrix for the motion of the particle regime at constant concentration is formed by the curve of unstable steady states of the particle and by the parts of tangent lines of infinite slope to the curve of stable steady states (in points limiting the interval of existence of two stable steady states of the particle — Fig. 6, dashed line). If the state of the particle is situated above the separatrix, the particle temperature is

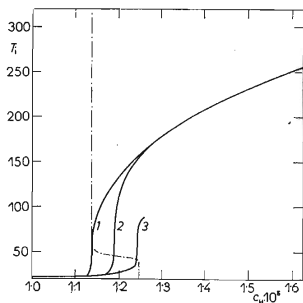


Fig. 7

Dependence of Catalyst Particle Temperature ($^{\circ}\text{C}$) on Hydrogen Concentration in the Bulk of Reaction Mixture (mol/cm^3) for Various Initial Hydrogen Concentrations in Mixture

Dashed and dotted line is the separatrix, 1 $c_{\text{H}_0} = 1.59 \cdot 10^{-6}$, 2 $1.3 \cdot 10^{-6}$, 3 $1.19 \cdot 10^{-6} \text{ mol}/\text{cm}^{-3}$.

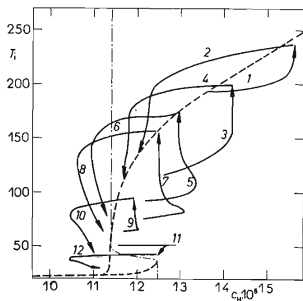


FIG. 8

Example of Experimental Dependence of the Catalyst Particle Temperature ($^{\circ}\text{C}$) on Hydrogen Concentration in the Bulk of Reaction Mixture (mol/cm^3) at a Step Change of Hydrogen Concentration in the Inlet Mixture for 20°C .

Initial hydrogen concentration in mixture before the change was $1.61 \cdot 10^{-6} \text{ mol}/\text{cm}^3$, after the change $1.24 \cdot 10^{-6} \text{ mol}/\text{cm}^3$. Symbols used are the same as those used in Fig. 6.

moving spontaneous toward the temperature on the diffusion branch, if it is below the separatrix, it approaches the temperature on the kinetic branch.

In the cascade of mixed reactors a very interesting effect appears at the beginning of its operation. All reactors of the cascade are at the beginning of the operation at the temperature of the reactor bath (zero temperature difference between the particle and the bulk of the reaction mixture). At the motion of the regime at the constant concentration all trajectories should be oriented to the kinetic branch (as long as it exists). This means that in the region of existence of two stable steady states of the particle would be, at the same concentration, occupied only the kinetic branch; in the diffusion regime would operate neither reactor of the cascade. But in the region of existence of two steady states in the cascade of reactors part of the cascade can operate also on the diffusion branch of the curve of steady states. This is due to each reactor of the cascade being exposed at first to a higher concentration then is the concentration in steady state. At the start of the reaction the reaction mixture is passing at first over cold particles of the catalyst at which the reaction rate is low. Some reactors start the reaction at the concentration at which exists only the state

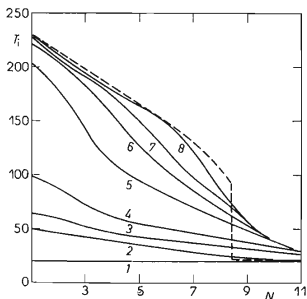


FIG. 9

Examples of Experimental Temperature Profiles of Catalyst Particles ($^{\circ}\text{C}$) Along the Tubular Reactor in Steady State and at Steadying Into this State at 20°C and Initial Hydrogen Concentration in the Mixture $1.59 \cdot 10^{-6} \text{ mol/cm}^3$

Dashed line is the dependence in steady state, solid line at steadying. $1 t = 0$ (initial state), $2 0.125$, $3 0.175$, $4 0.250$, $5 0.50$, $6 0.75$, $7 1.00$, $8 1.50 \text{ min}$.

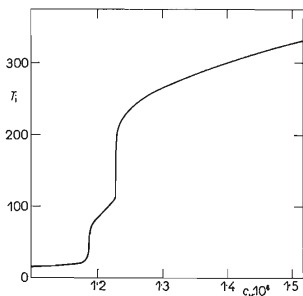


FIG. 10

Effect of Catalyst Deactivation on Temperature Dependence of Catalyst Particles ($^{\circ}\text{C}$) on Hydrogen Concentration in Mixture (mol/cm^3) for 10°C and Initial Hydrogen Concentration in Mixture $1.51 \cdot 10^{-6} \text{ mol/cm}^3$

on the diffusion branch even though they transfer into the region of existence of two steady states later. This enables the particle regime to "bypass" the separatrix and to reach the state on the diffusion branch. From results of measurements follows that as soon as the inlet concentration of the cascade is smaller than the highest concentration of the region of existence of two steady states of the particle, all reactors of the cascade transfer into the lowest *i.e.* the kinetic state only. If the inlet concentration is higher, in the region of existence of two particle states, a section forms in which the reactors of the cascade operate in the diffusion regime. The width of this region depends on the distance of the initial concentration from the concentration limiting the region of two steady states of the particle. The higher is the difference of both these concentrations, the greater is the part of the diffusion branch belonging into the discussed section. At high inlet concentration the whole cascade operates in the regime corresponding to the diffusion branch (Fig. 7).

Opposite phenomenon takes place when the catalyst particles in the initial state have higher temperature than in the steady state. The reaction mixture is passing at first over the hot particles and the reaction rate is high. In the next reactors of the cascade are therefore the catalyst particles exposed to the mixture of lower concentration than corresponds to the steady state. The curve of motion of the reactor regime is bypassing the separatrix from the other side. Though this was not experimentally confirmed it is not possible to exclude formation of the section in which the particles are on the kinetic branch in the region of existence of two steady states of the particle. An interesting phenomenon was thus confirmed that cooling of the catalyst particles before the beginning of the reaction may lead to the transfer of the particle regime into the diffusion region and *vice versa* the heating of particles before the beginning of the reaction may lead to transfer into the kinetic regime. As long as the inlet concentration is smaller than the highest concentration in the region of existence of two steady states this phenomenon cannot take place. The behaviour of the cascade of reactors is therefore simple. If the catalyst particles before the beginning of the dynamic operation are cold, the regime transfers to the kinetic branch, if they are warm it transfers to the diffusion branch. Examples of measured results are given in Fig. 8.

Axial Temperature Profiles of Catalyst Particles in Tubular Reactor

From the experimental data it is possible to obtain information on the temperature changes of the catalyst particles along the tubular reactor at the assumption that the number of reactors of the cascade is proportional to the length coordinate of the tubular reactor. In Fig. 9 examples are given of axial temperature profiles of particles (the number of passage of the reaction mixture through the reactor is given by the number of the reactor of the cascade). The experimental dependences are slightly distorted by the effect of axial mixing of the mixture in the tube of the bypass and the reactor.

This distortion is obvious especially at concentration profiles which cannot be for this reason reliably interpreted.

The Effect of Water on the Catalyst Activity

It was observed in the measurements that the behaviour of the catalyst is profoundly affected by adsorption of water vapours. When the catalyst was exposed to the reaction mixture of low hydrogen concentration at low temperature, the originating water was adsorbed and decreased the catalyst activity. By increasing the hydrogen concentration, the particle was heated autothermally and water at temperatures above 50 to 60°C was desorbed. The adsorption and desorption of water is not instantaneous and so adsorption of water affects the dynamic behaviour of the particle as well. For elimination of the effect of water desorption the particle was before the beginning of the experiment heated to a high temperature by introducing the reaction mixture of high hydrogen concentration. The interesting effect of water adsorption on the behaviour of the catalyst was observed on the particle poisoned by sodium hydroxide. In this case a double transfer of the reactor regime was found at the decreasing of the hydrogen concentration in the mixture. The first transfer was caused by transfer from the diffusion regime into the kinetic one (autothermal effect), the second transfer by the change of the kinetic regime at temperature when water is not adsorbed into the kinetic regime with strong effect of water adsorption. On the little active catalyst (poisoned by water) these two transfers can be distinguished since the temperature of transfer into the diffusion regime is higher than the temperature at which water is desorbed (Fig. 10). The transfer from the diffusion branch to the kinetic one on an active catalyst takes place at temperatures at which water already begins to be adsorbed.

LIST OF SYMBOLS

c_H	hydrogen concentration in the bulk of reaction mixture (mol/cm ³)
c_{H0}	hydrogen concentration in the bulk of reaction mixture at the beginning of the dynamic operation (mol/cm ³)
N	number of individual passage of the reaction mixture through the reactor
t	time (min)
T	temperature of the bulk of the reaction mixture (°C)
T_1	temperature of the catalyst particle (°C)

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