CATALYTIC PROCESSES UNDER UNSTEADY-STATE CONDITIONS

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PREFACE

It is often taken for granted that only invariable conditions,
chemical in particular, will guarantee the efficiency of a
technological process. This, of course, does not refer to
processes which are "unsteady" by nature, e.g. to those
involving relatively high rates of catalyst deactivation and
which include periodicity in drying, crystallization, pressing or
baking of products, etc. Time-invariability of the processes'
parameters in large-scale production is usually achieved by
careful stabilization of the inlet conditions. Automatic or
manual variation of the inlet conditions helps to achieve the
optimum steady-state conditions assumed as appropriate on the
basis of tests, process simulation or, sometimes, intuition. If
needed, the technological regime of the process can be somewhat
corrected.

However, the optimum conditions of the process can be
achieved with the so-called non-steady-state operation (refs.
1-3) which involves variation of the inlet conditions. This
opens up wide possibilities to form concentration, temperature,
pressure and state fields, which are absolutely unobtainable
under fixed inlet conditions. Steady-state or quasi-steady-state
conditions may be realized only in a particular variant of the
non-steady-state regime, that is, when the rate of variation of
the inlet parameters is very low or cannot be detected at all
within an observable period of time. Thus, it is clear without
going into detail that the non-steady-state operation allows an
increase in the efficiency of the process in respect of the
productivity and selectivity, reduces power requirements and
costs to a far greater extent than does steady-state technology.

Recently, a number of theoretical and practical studies have
demonstrated the possibility of non-steady-state regime creation
for a large class of processes which can thus exceed the
efficiency of stationary regimes. Mass and heat transfer,
adsorption, rectification, separation of solid particles into
fractions and partition of liquid or gas mixtures on the

principle of dynamic separation are examples of such processes.
Forced pulsation combustion of solid fuels results in an
intensified oxidizing and heat exchange, which reduces the
energy consumption. It also allows for operation under
conditions of a slight excess of air or oxygen, decreases the
nitric oxide content and provides better cleaning of the heat-
-exchanging surface. The intensification of a process in which
mass and/or heat exchange plays an important role is often
associated with an increase in exchange coefficients under non-
-steady-state conditions at time when the frequency of the
initiated flow velocity pulsations is close to the natural
frequencies of turbulent pulsations. For example, the
investigation of the hydrodynamic situation in the granular
catalyst bed reveals two different regions of its void volume:
the region of mixing and disintegrating jets (the flow zone) and
the region with twirling and pulsating vortexes caused by
separation of the flow from the grain surface in the vicinity of
contact points (the non-flow-zone) (ref. 3). The vortex
pulsation frequency, ω , is directly proportional to the linear
velocity, u, and varies inversely with the grain diameter, d. If
the perturbation frequency at the bed inlet is initiated at a
value corresponding to $\omega \approx 0.5$ u/d, the flow (of gas or liquid)
becomes significantly turbulent and the intensity of exchange
between the zones is found to be more pronounced. All this
serves to improve the exchange between the flow in the void
volume and the external surface of the bed's particles.

An increase in the heat-transfer coefficients of the shell-
-and-tube heat exchanger is explained by an increase in
turbulence when forced pulsations of mixture flow are initiated
at the inlet. Owing to the non-linear dependence of the froth
thickness on the gas velocity in the distillation tower, the
pulsating flow foams significantly, thus extending the contact
time of the phases and increasing the efficiency of the process.

Another reason leading to a higher performance of the mass-
-exchange apparatus under non-steady-state operation is an
increase in the motive force. The essence of this phenomenon for
a plate-type or packed apparatus lies in the fact that with
cyclic draining (complete or partial) of liquid from a catalytic

stage and with its relatively fast replacement by a fresh
mixture, the regime created approaches one of piston flow
characterized by the maximum possible motive force. The most
intensified regime in the apparatus is achieved when the period
of the cycle is about the mean residence time of liquid at the
stage (ref. 4).

Application of forced non-steady-state conditions in
polymerization processes leads to the alteration of distribution
functions of polymer molecular weights and to an increase in
the reactor productivity compared to steady-state operation
(refs. 5-6). It may take place, for example, in the case of
periodic variation of the inlet hydrogen concentration in the
free radical condensation polymerization of olefins on a
Ziegler catalyst. A change in the distribution of molecular
weights follows. Experiments, for example, on the radical
polymerization of styrene (ref. 6) as well as on ethylene and
propylene polymerization (ref. 7) have confirmed many
theoretical conclusions. Irradiation of the reaction zone
during the radical polymerization can periodically create high
concentrations of primary radicals which may set a limit to the
length of the polymer chains and cause narrow-dispersion peaks
in the molecular weight distribution.

Some authors (refs. 8, 9) have reported peculiar
applications of non-steady-state regimes to complex biological
systems where it proved possible to stabilize the coexistence of
two competing populations, while under steady-state conditions
one population was likely to be eliminated.

One of the challenges in apparatus design, especially of
reactors of large unit power, is the requirement to provide
homogeneous hydrodynamic, heat and concentration conditions
inside the reaction volume. Pilot and industrial research
connected with pulsating-type apparatus for the processes of
extraction, sorption, dissolution, leaching, phase mixing, etc.,
has demonstrated the high efficiency of forced hydrodynamic
non-steady-state processes which include a liquid phase (ref.
10).

The efficiency of the forced non-steady-state regime is
clearly revealed upon consideration of the ideal mixing

converters for reactions of the second order (ref. 11). Reactor
productivity might be stepped up even further if not only the
composition but also the flowrate were subject to periodic
variation and especially if the peak values of their pulsations
are out of phase. The non-steady-state regimes appeared to be
most efficient when the expressions of chemical conversion rates
have extreme properties or if the reactions are reversible. One
of the best ways to ignite a non-steady-state process is thought
to be the heat-transfer agent, though this has proved of little
use for a number of processes. An increase in selectivity of
continuous catalytic reactions in a reactor with ideal mixing
can be attained if the orders of the main and the side reactions
vary.

Transition to forced non-steady-state regimes in the gas-
-solid system would be expected to result in a considerable
rise in the efficiency of roasting of non-ferrous ores in
metallurgy (ref. 12) and in the interaction of solids with
oxygen in the gas phase (ref. 13), where ignition of the system
is performed by variation of the initial oxygen concentration.

An heterogeneous reactor with a solid-particle catalyst
represents a dynamic system in which complex processes are
united in space and time. These processes are carried out inside
and on the surface of the porous catalyst and both inside and
along the boundaries of the reaction volume. All flows under
steady-state conditions are united by material and energy
balances. That is why it is not often possible to arrange for a
catalytic process to operate with all its components (from the
catalyst surface to the contact section) in the optimum regime.
The composition, structure and properties of the catalyst are,
for example, determined by the condition of the gas phase.
Consequently, it does not seem possible radically to affect the
properties of the catalyst operating under steady-state
conditions, since the gas phase composition is predetermined by
the extent of conversion and selectivity. The non-steady-state
regime allows for periodic variation of the gas phase
composition or catalyst activation to such an extent that the
catalyst's condition can be quite different from that in the
steady-state regime and average process efficiency will be
considerably increased. Of course, all balance relationships

will also be preserved but only in an average period.

The reader may want another illustration. During a reversible exothermic process in a reactor with a fixed catalyst bed, the temperature increases monotonically along the catalyst body and is linearly dependent on the extent of conversion. The optimum regime, however, requires a reduction of the temperature with increasing extent of conversion, but this cannot be achieved because of the adiabatic conditions of the process. To overcome this difficulty, many reversible exothermic processes, e.g., sulphur dioxide oxidation in the production of sulphuric acid, synthesis of ammonia and methanol, sulphur production by the Clauss method, carbon monoxide conversion, are in practice carried out in several adiabatic catalyst beds placed in series, with intermediate removal in the reaction heat. It will be shown further in this book that organization of the forced non-steady--state conditions for these kinds of processes allows for a temperature decrease with increasing extent of conversion. It will thus permit reversible processes in one catalyst bed.

This book is a natural logical continuation of "Unsteady Processes In Catalytic Reactors" published in 1985 by Elsevier Science Publishers and represents an attack on the theoretical principles and methods of practical organization of hetereogeneous catalytic reactions under forced non-steady-state conditions. Its contents fall into two parts. The first part (chapters 1 - 6) deals with the theoretical basis of the methods assumed as reasonable for operation of the catalytic processes under non-steady-state conditions. Attention is mainly focused on the non-steady-state of the catalyst, formation and motion of a heat front in a fixed granular catalyst bed and organization of the catalytic processes in the reaction mixture flow reversal regime in the fixed catalyst bed. The second part (chapters 7 - 9) considers plans and realization schemes for important industrial processes under forced non-steady-state conditions. Oxidation of sulphur dioxide in sulphuric acid production, detoxication of exhaust-diluted substances and carbon monoxide, and production of high-potency heat from slightly concentrated gases will be discussed in detail.

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Chapter 1

REACTION PERFORMANCE IN THE CATALYST UNSTEADY STATE

1.1 UNSTEADY STATE OF THE CATALYST

According to Academician Boreskov's definition of catalysis
(ref. 1), it is an acceleration of a chemical reaction over
certain substances (called catalysts) which repeatedly interact
with reagents without entering into the composition of the
product. A catalytic process usually involves three successive
stages: adsorption of initial components, chemical conversion on
the surface and desorption of the reaction product. Each stage
consists of consecutive or parallel steps of both physical and
chemical interaction of intermediate compounds on the surface
as well as with the components of the gas phase. Regardless of
its specific action, the nature of catalysis is common and can
be defined as follows: the catalyst, being a part of the
intermediate compounds, increases the degree of compensation of
the energy required for the splitting of old bonds by the energy
released in the formation of the new bonds. This results in a
decrease in the activation energy of the chemical reaction. That
is, in short, an up-to-date point of view to the considerable
growth of the chemical transformation rate in catalysed
reactions.

The state of the catalyst is affected by the reaction medium.
To every gas phase composition invariable over a lengthy period
of time, catalyst surface temperature and initial conditions
there corresponds an unique catalyst state, characterized by
specific structure, composition and catalytic properties,
provided there is no external-diffusion resistance. This
catalyst state, of which time-invariant activity and selectivity
are characteristic, does not, however, always prove optimal. One
can imagine a situation, e.g., periodic variation in some range
of gaseous mixture composition when the unsteady catalyst
activity and selectivity exceed on average those under the
steady state. It is recommended to compare catalyst states at
identical concentrations both under stationary and averaged non-
-stationary conditions. The efficiency of a catalytic process
under forced non-steady-state conditions is determined by the

.mechanism of the process, the rate constants of various reaction stages and the dynamic properties of the catalyst surface. Therefore, it makes sense briefly to remind the reader of those properties (ref. 2) and then proceed to the problems concerned with the performance of the processes in the unsteady state of the catalyst surface.

The chemical composition of the catalyst, its surface structure and catalytic properties undergo some changes as the result of variation of the reaction medium. Numerous experimental data confirm that the composition, structure and properties of different catalysts, massive and supported metals and alloys, simple and complex oxides and acid-base catalysts really are influenced by the concentrations of the components in the reaction mixture and temperature (ref. 3).

The modification of the chemical composition and the change in the catalytic properties in many cases are distinct as, for example, in sulphur dioxide oxidation on vanadium (ref. 4). The metal oxidation state decreases from V^{5+} to V^{4+} with increasing concentration of SO_2 in the reaction mixture and decreasing temperature. These variations are reversible and have small relaxation times. Furthermore, at low temperatures with a reaction mixture enriched with SO_2 and long period of interaction with the catalyst, a special state of inactive quadrivalent crystalline vanadium appears. Its concentration is in good agreement with the decrease in catalytic activity. These types of variations are characterized by longer relaxation times.

A considerable transformation in the chemical composition and catalytic properties under the influence of the reaction medium is also observed for solid catalysts, for example, for oxidation of CO on various manganese oxide catalysts (ref. 5). The surface composition of the catalyst with different initial composition in the steady-state regime corresponds to the one and the same catalyst structure which can only exist in this reaction medium. Similar steady states of manganese oxides could be obtained after 30 hours of catalyst treatment by the reaction mixture at 230°C. The same results were obtained for oxidation of CO on copper-containing catalysts (ref. 6). Interaction of these catalysts with the reaction mixture involved a relatively rapid

change in the oxidation state of the catalyst surface and its underlayer and also significantly slowed the creation or destruction of the space defects (inhomogeneities), which are evidently connected with phase rearrangements of the surface layer.

As was shown for conversion of CO on copper-containing oxide catalysts, the oxidation of the catalyst by water vapour affects the catalytic activity. In this case, the stationary concentration of oxygen is attained much more slowly as compared with the catalytic reaction itself (ref. 7).

The changes in the oxide catalyst properties under the influence of the reaction medium is evidently the most studied aspect of the variety of heterogeneous catalytic processes. The oxidation state of the catalyst is decreased following the reduction of this ratio and this results in a sharp drop in the general reaction rate, while the selectivity toward the incomplete oxidation product is simultaneously increased. Acrolein oxidation to acrylic acid on a vanadium-molybdenum oxide catalyst is the perfect example of the above mentioned change in parameters (ref. 8).

The effect of the reaction mixture has also been observed for acid-base catalysts. For example, under the influence of water vapour, the extent of hydration of acidic centres and also the ratio between the Brönsted and Lewis centres can be changed.

As reported for metallic catalysts, their surface is easily reconstructed under the influence of the reaction medium and tends to maximum surface energy. Very often the reconstructive adsorption of reactants leads to a change in the structure of the metal surface (ref. 9). Moreover, the composition of the near-surface layer is usually also modified as a result of dissolution of the reaction mixture components. The amount of the components adsorbed is often many times greater than a monolayer coverage. Levchenko et al. (ref. 10) observed a slow change in the rate of ethene oxidation on silver, which they related to oxygen diffusion in the near-surface layer of the catalyst. A similar process was observed in the catalysed oxidation of hydrogen on silver films (ref. 11). All these factors result in a change in the sorption heat of the reactants

on the metal surface and in the activation energy of elementary steps. Consequently, the total catalytic activity and selectivity of the reaction are changed.

The surface composition of solid alloys is also modified under the influence of the reaction medium. The free surface energy is changed due to the chemisorption and, therefore, it is more advantageous for the alloy component with the higher chemisorption energy to be on the surface. As reported in ref. 12 for Pt-Sn alloys, in a vacuum their surface is enriched with tin (compared to the catalyst bulk), whereas in a carbon monoxide atmosphere it is enriched with platinum. Atom shift in metals is usually limited to the thin near-surface layer, but with an increase in temperature the thickness of this layer may grow.

We have only considered some examples of a large body of experimental data. These data taken together permit one to conclude that solid catalysts are components of the reaction system and are sensitive to variations of the reaction mixture composition, temperature and other parameters. To each composition and temperature of the reaction mixture, there corresponds a certain catalyst steady state.

Some experimental data obtained about 30 years ago demonstrate the existence of hysteresis in the rate of a chemical reaction. Recently, isothermal self-excited oscillative regimes on the catalyst surface at invariable gas phase composition were discovered. This does not invalidate the above deduction, but only indicates that the steady state of the catalyst is determined by the composition and temperature of the gas phase as well as by the changes in the condition of this phase.

The influence of the reaction mixture on catalyst properties must be taken into account in the kinetic dependences of the reaction in heterogeneous catalysis. In the vast majority of cases, kinetic equations are usually derived on a tacit assumption that the composition of the solid catalyst and its properties are independent of the reaction mixture composition and of its influence on the catalyst. In reality, this condition is not fulfilled because the chemical composition of