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Unsteady catalytic processes and sorption-catalytic technologies

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Abstract. Catalytic processes that occur under conditions of the targeted unsteady state of the catalyst are considered. The highest efficiency of catalytic processes was found to be ensured by a controlled combination of thermal non-stationarity and unsteady composition of the catalyst surface. The processes based on this principle are analysed, in particular, catalytic selective reduction of nitrogen oxides, deep oxidation of volatile organic impurities, production of sulfur by the Claus process and by hydrogen sulfide decomposition, oxidation of sulfur dioxide, methane steam reforming and anaerobic combustion, selective oxidation of hydrocarbons, *etc*. The bibliography includes 234 references.

I. Introduction

Catalytic processes operating under targeted unsteady state conditions receive considerable attention in both the scientific research and industry. The reason for such keen interest lies in the fact that unsteady-state conditions allow one to enhance the efficiency of catalytic technologies, namely, accelerate reactions, enhance their selectivity, increase the yields of the target products, decrease the energy consumption and reduce the operational expenses and the cost of reactors.

None of the known heterogeneous catalysts represent a true unsteady system during its operation. At the very least, this is associated with their inevitable deactivation, which shortens their service life and necessitates their replacement or regeneration once the service life is overrun. Nonetheless, two conceptually opposite approaches are distinguished, namely, a steady-state approach that postulates the time invariability (as far as possible) of all process parameters and the unsteady approach based on the targeted dynamic variation of these parameters. The present review is exclusively devoted to catalytic technologies that employ catalysts under the targeted unsteady-state conditions and demonstrate substantial advantages over analogous stationary processes.

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In the recent decades, the most significant progress in unsteady catalysis was associated with the reverse-flow processes. The latter are based on concepts of the thermal non-stationarity that arises in a fixed adiabatic catalyst bed as the parameters of the reaction mixture flowed through this bed are modulated. However, it is evident that the progress in this field lies in the development of processes with not only the modulated catalyst temperature but also with the modulated chemical composition of the surface.

The present review considers mainly the gas-phase reactions that occur on the solid catalyst surface. Apparently, the formulated approach can also be applied to multiphase catalytic processes; however, this field is very wide and deserves special consideration.

Insofar as the periodic changes in the catalyst state are directly associated with the sorption, most of processes considered below can be described as sorption-catalytic processes, which implies that it is joint sorption and catalytic processes that occur within one catalyst bed or a single process vessel. This approach does not embrace the combinations of catalytic and sorption processes that are carried out separately and independently in different reactors even within one flow scheme.

In this study, sorption is understood in the general sense, *i.e*., as the reversible physical adsorption of reactants, their reversible (irreversible) chemisorption associated with chemical reactions and the formation of stable intermediates on the active surface or even as the absorption of reactants in a liquid film of the active component melt.

The first studies of cyclic catalytic processes that involved the periodically modulated catalyst state date back to the 19th century. The analysis of the development of these studies leads to a paradoxic idea that in a certain sense, the first catalytic processes studied were cyclic unsteady processes.

This can be illustrated by several examples. Thus the English chemist Claus [1,2] studied the reaction of hydrogen sulfide oxidation to sulfur, which opened up the way to the recovery of elemental sulfur from hydrogen sulfide, in fact, first under the adsorption-catalytic conditions (with the adsorption of liquid sulfur on the catalyst). Somewhat earlier, his compatriot Deacon [3–5] discovered the reaction of hydrogen chloride oxidation with oxygen, which marked the beginning of the catalytic processes for the commercial synthesis of chlorine. Unlike Claus, he did not deal with unsteady technologies but, on the contrary, proposed and carried out a stationary

catalytic process. However, this very fact indicates that the periodic processes preceded his studies.

The same year that his patent was issued,[3] the unsteady methane steam reforming in the presence of a sorbent that absorbed CO_2 was described .[6] This study is considered as the pioneering in the catalytic steam reforming of hydrocarbons.

Many other examples of similar studies carried out since the end of the 19th century to the first half of the 20th century can be mentioned.

Such a development, which, at the first glance, looks paradoxic, however does not lack logics. In their early stage, the studies of the periodical combination of the known chemical reactions could be reduced to the closed reaction cycles, actually, to the stationary catalysis, which, at that time, was of significant interest for practice. Scientific research was also directed towards the stationary catalytic processes as more predictable, reproducible and hence more attractive for their exploration and building up the relevant theories.

Later, with the accumulation of knowledge on the catalytic processes, the limitations inherent in the stationary catalysis and narrowing the freedom of developers of new technologies were revealed. That is why attention was redirected to the 'origins', *i.e.*, the unsteady catalytic processes but with the new insight into the already known phenomena.

Systematic studies of the unsteady phenomena in catalysis date back to the second half of the 20th century. After the first publications on the unsteady modes of operation of catalytic reactors, which appeared in the 1960s,[7–11] the rapid progress in this field (both experimental[12–16] and theoretical[17–20]) was observed.

The studies[21–29] carried out under supervision of academician G K Boreskov and Yu Sh Matros at the Institute of Catalysis of the Siberian Branch of the Russian Academy of Science have made a considerable contribution into the theory and practice of unsteady catalysis. These studies have given the first physical explanation and substantiation to the observed phenomena, being particularly based on the Boreskov' concept of the changes in the catalyst state under the reaction conditions.

II. Theoretical basis and methods for organisation of unsteady-state conditions in catalyst beds

Any heterogeneous catalytic reaction includes several separate stages that can be associated with successive chemical and sorption processes. Obviously, under steady-state conditions, the rates of these stages are related by rigid balance relationships, which sometimes limit the efficiency of the process.

Under unsteady-state conditions, a set of stages can be represented as separate cycles, which are technologically isolated in the space and/or time. Such conditions make it possible to weaken or violate, at least theoretically, the local balance relationships mentioned above. This eliminates a part of restrictions and opens up additional possibilities for the development of new technologies.

Obviously, the disintegration of reactions into individual cycles implies that the latter form a closed system. In other words, a series of cycles should provide the return of the catalytic system into its original state in order to ensure their repetition. Otherwise, the system cannot be considered as catalytic. Moreover, the closed nature implies the observance of the integral mass and energy balances in the overall process cycle.

The rates of reaction and sorption processes involved in the catalytic cycle and their ratio are determined by the nature of the active catalyst surface and reaction mixture components and also by the external conditions (reaction mixture composition, temperature, pressure). Hence, the realisation of unsteady-state conditions is associated with the choice of an appropriate catalyst–sorbent and with the cyclic time variations of at least one of external factors.

1. Temperature modulation

The effect of temperature modulation as a source of the unsteady state in catalytic systems was discussed in numerous scientific studies. Their most important result was the development of catalytic reverse-flow processes,[22, 25, 30, 31] which have found wide use in the industry. Reverse processes involve no direct control over the temperature, and their thermal non-stationarity is caused by the motion of thermal waves in the motionless adiabatic catalyst beds under the conditions of the periodic reversal of the direction of the initial filtrating gas mixture with a low inlet temperature.

Figure 1 shows examples of flow schemes of reverse processes. In the simplest case (Fig. 1 *a*), a system of switching valves changes the flow direction of the reaction mixture in the catalyst bed. In a modified scheme shown in Fig. 1 *b*, the catalyst in the edge parts of the bed is partially replaced by a heat-regenerating material (inert), which is catalytically inactive. Figure 1 *c* shows a multibed scheme (for the sake of simplicity, only two beds are shown) in which the inlet or outlet of both heat and mass (heating/cooling of the flow, inlet/outlet of additional flows and reagents) takes place between the fragments of the catalyst bed. A valve-free version of the reverse process is known, which includes the rotating beds packed with the catalyst and the inert material (Fig. 1 *d*).

Figure 2 shows certain interesting flow schemes is which the thermal non-stationarity in the catalyst beds may be created without the reversal of the reaction flow.[22]

It is important to understand that for processes involving the thermal non-stationarity of the catalyst, one faces the problem of the basic approach to the development of such technologies rather than of the unsteady chemical composition of the catalyst.

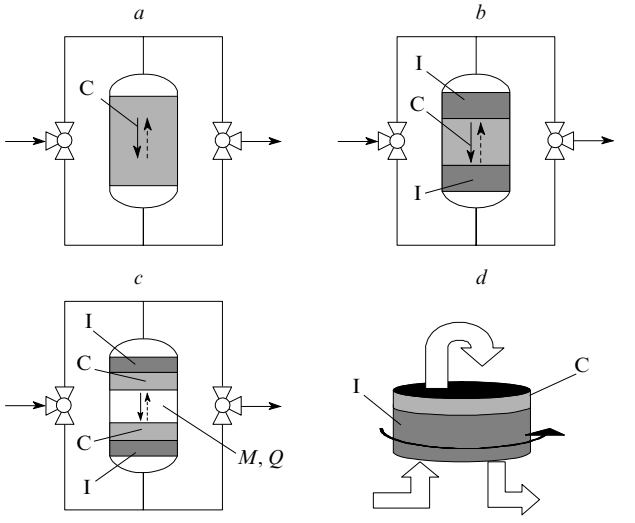


Figure 1. Flow schemes of reverse processes.
(*a*) A one-bed scheme, (*b*) a scheme inert–catalyst–inert, (*c*) a multibed scheme with intermediate heat exchange and inlet/outlet of flows, (*d*) a scheme with rotating beds; dark arrow shows the direction of rotation of the catalyst bed, light arrows show the directions of the reactant flows. Here and in Fig. 2, solid and dashed arrows show the directions of the reaction flow in different phases of the cycle; C is the catalyst; I is an inert heat-regenerating material; *M*, *Q* are the inlet/outlet of reactants and heat, respectively.

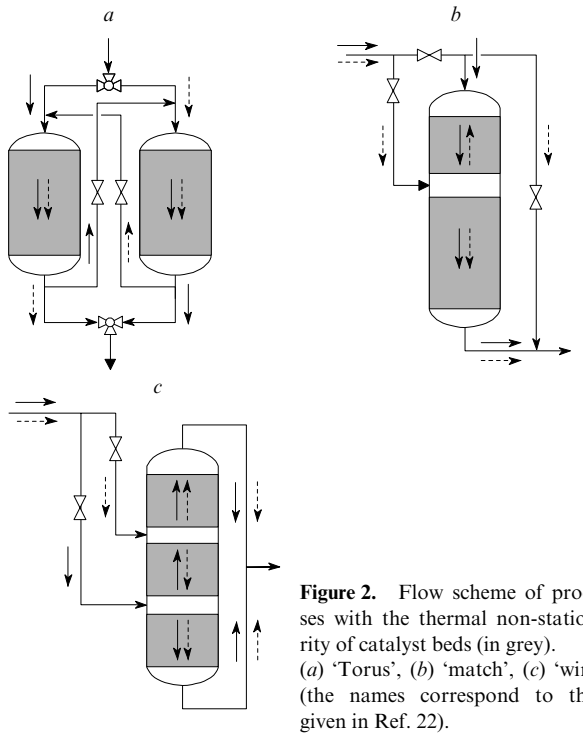


Figure 2. Flow scheme of processes with the thermal non-stationarity of catalyst beds (in grey). (*a*) 'Torus', (*b*) 'match', (*c*) 'wings' (the names correspond to those given in Ref. 22).

2. Modulation of the reaction mixture composition

A comprehensive review of the studies on unsteady isothermal modes under forced modulation of the reaction mixture composition is given in Ref. 32. As a rule, the effectiveness of periodic modes is compared with the parameters of equivalent stationary modes in which the reactant concentrations are equal to the cycle-averaged concentrations in the unsteady mode.

In simple reaction mixtures with virtually one reaction route (CO oxidation,[33–47] hydrogenation of ethylene [15,48] and aromatic hydrocarbons,[49–51] methanation of carbon oxides,[52–54] syntheses of methanol [55–57] and ammonia,[58–63] SO_2 oxidation,[16,64] the Claus reaction,[65] synthesis of ethyl acetate from ethylene and acetic acid,[66–68] deamination of primary amines and dehydration of alcohols, [69–72] *etc.*), the main positive effect of the optimum unsteady mode lies in the increase in the cycle-averaged reaction rate. However, for the majority of simple reaction systems, the rate increase was no more than 1.5–2-fold, which can hardly be considered quantitatively significant. At the same time, it should be noted that for the SO_2 oxidation under isothermal conditions with periodic alteration of the SO_2-containing mixture and air feeding,[64] the average yield of sulfur trioxide can exceed the equilibrium limit in the equivalent stationary mode.

Modes with periodic modulation of the reactant concentrations in systems with complicated parallel-sequential processes are more interesting.

According to theoretical studies, for the periodic modulation of the mixture composition in a model system of two parallel reactions, the selectivity of the target conversion can change if the reactions have different orders with respect to reactants,[17] whereas in a model system of three sequential reactions in a perfect-mixing reactor, the selectivity with respect to the intermediate product can increase.[73] Matros *et al.*[21–28] carried out a comprehensive systematic analysis of unsteady modes of complex reactions. They have found that the gain in the selectivity of processes carried out in unsteady cyclic modes substantially depends on the reaction mechanism and the type and parameters of unsteady modes. Moreover, they have shown that the adequate description of such systems requires the use of unsteady kinetic models that take into account the dynamics of adsorption processes and the changes in the catalyst surface state under the reaction conditions.

The possibility of the enhancement of the reaction selectivity and the increase in the yield of the target products and of the reduction of the side-product yields was experimentally demonstrated by the example of several complex processes such as the NO reduction under the action of CO,[74–80] selective hydrogenation of butadiene [81] and acetylene,[82,83] oligomerisation of methane and ethylene,[84–88] oxidative dimerisation of methane,[89–92] oxidation of ethylene to ethylene oxide [93,94] and propylene to propylene oxide,[95] oxidative and steam reforming of methane into the synthesis gas,[96–98] oxidation of propylene to acrolein,[99–102] anaerobic oxidative dehydrogenation of hydrocarbons (propane to propylene, butane to butene and butadiene, butene to butadiene),[46,103–109] oxidation of butane to maleic anhydride, of aromatic hydrocarbons to maleic and phthalic anhydrides, synthesis of aromatic nitriles, the Fischer–Tropsh reaction,[32] *etc.*

For all these reactions, the positive effect was observed only in a limited range of characteristics of unsteady modes (cycle duration, amplitude of concentration oscillations, phase shift in the supply of reactants, *etc.*). As an example, a system for the catalytic purification of automotive exhausts can be considered. Its peculiarity consists of the fact that the unsteady composition of the original reaction mixture is determined by the specifics of the engine operation. Under the conditions that did not allow one to control the system and optimise the parameters of unsteady modes, both positive and negative effects of the non-stationarity could be observed,[110–113] and its overall effect was ambiguous.[32]

Figure 3 shows flow schemes that makes it possible to realise periodic modulation of the reaction mixture composition and/or the separate delivery of reactants. In the simplest case (Fig. 3 *a*), the modulation of the composition was achieved by the alternating supply of individual reactants or reaction mixtures of different composition. Such a process is basically periodic. To provide the overall continuity in the composition modulation, a scheme that includes two (and more) reactors (Fig. 3 *b*) with the alternating cyclic supply of reactants and the processes with moving or rotating catalyst beds (Figs 3 *c*,*d*) were used. In the latter case, different reactants are permanently delivered into different reactors and transported in their sorbed state by the catalyst, which permanently travels between the reactors.

3. Chromatographic mode of catalytic reactions

Reactive chromatographic processes with the periodically varied composition of the mixture form a subclass of unsteady processes.[114–117] They were pioneered by Roginskii back in the early 1960s.[7–9] In these processes, advantage was taken of the adsorption properties of catalysts, which allow one to carry out chromatographic separation of the reaction mixture simultaneously with chemical transformations. The merits of these technologies include the possibility of separate extraction of individual products and the achievement of superequilibrium degrees of conversion due to the dynamic separation of components in the catalyst bed.

The chromatographic mode is based on the pulsed supply of the reaction mixture (pulsed delivery of reactants into the inert-gas flow or pulsed introduction of one component into the flow of another reactant) and can be implemented in a one-reactor scheme (see Fig. 3 *a*). A multibed scheme with the constant direction of the reaction mixture flow in beds and the periodical shift of the points of the reactant inlet and the product outlet, which provides the permanent circulation of the adsorption and reaction waves in catalyst beds, deserves attention [118] (Fig. 4). Such a system, which received the name

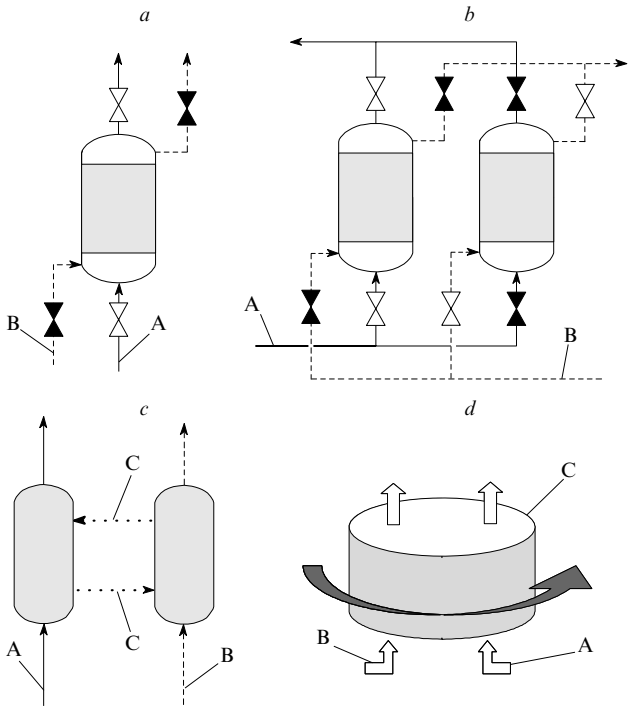


Figure 3. Flow schemes of modes with modulation of the reaction mixture composition.
(*a*) One-reactor periodic process; (*b*) two-reactor continuous process, valves in different positions that correspond to different phases of the process are marked in white and black; (*c*) two-reactor process with the moving catalyst bed; (*d*) process with rotating catalyst bed. A and B are different reactants or mixtures of different composition, C is catalyst.

Simulated Moving Bed Reactor (SMBR), holds much promise for carrying out certain practically important reactions.[114]

It should be noted that a reactive chromatography process is efficient under the high residence time of the reaction mixture in the reactor, *i.e.*, in case of high loading volume of a catalyst with low specific productivity. Obviously, it is economically more reasonable to use the reactive chromatography only in small-scale processes of fine organic synthesis, where the highly expensive reactants and products determine the high capital and production costs.

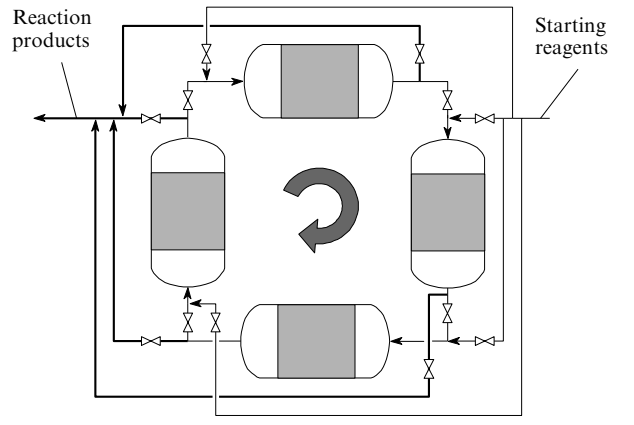


Figure 4. Flow scheme for a reactive chromatography process with pseudomoving catalyst beds.
The arrow in the centre shows the direction of shift of inlet points of reagents and outlet points of reaction products.

4. Periodic pressure modulation

Periodic pressure modulation or the impact of periodic pressure pulses on the reaction system represent an alternative method for the creation of unsteady-state conditions in catalytic reactions. Here, two groups of processes should be distinguished, namely, at low and high frequencies of pressure oscillations.

The first group includes the processes with the cycle duration from several tens of seconds to several minutes. They combine the pressure swing adsorption (PSA) process, which was known since the early 1960s,[119] and a catalytic reaction. Such processes are called pressure swing reactions (PSR) processes. Their efficiency was demonstrated in model studies [120, 121] and also by the example of methane steam reforming in the presence of substances that absorb CO_2.[122]

The second group includes the processes generated by high-frequency pressure pulses (from tenth fractions to several tens and hundreds of Hz). Studies of such processes were surveyed by Silveston and Hudgins.[123] Pressure oscillations intensify mass transfer in the catalyst pores, which, on the one hand, can accelerate the reactions in simple reaction systems and, on the other hand, change the selectivities and yields of products and the other parameters in complex systems. Presumably, such pulses can induce oscillations in the reactant concentrations on the catalyst surface, which may affect the reaction rate and selectivity.

Pressure pulses can be generated both by an external source or be induced by mechanical oscillations in catalytic systems. Particularly, as was shown theoretically, the periodic pressure modulation with a frequency of an order of magnitude of several hundreds and thousands of Hz can arise in the channels of a block catalyst as a result of spontaneous turbulisation of the gas flow at the entry of channels in the presence of surface irregularities on the frontal panel of the unit.[124]

III. Catalytic processes that utilise the unsteady states of catalyst

In this Section, attention is focused on the technologies that purposefully utilise the unsteady state of a catalyst. The described processes are based on the combined action of thermal and adsorption unsteady factors.

1. Selective catalytic reduction of nitrogen oxides

As the example of the targeted use of the unsteady state of a catalyst, the NOx reverse process can be mentioned, which was developed [30, 125, 126] at the Institute of Catalysts of the Siberian Branch of the Russian Academy of Sciences based on the principle of the periodic reversal of the reaction mixture flow for the reduction of nitrogen oxides according to the reaction

$$NO_x + NH_3 \longrightarrow N_2 + H_2O. \quad (1)$$

At the Biysk Oleum Plant, a commercial-scale unit has been developed for the reduction of nitrogen oxides from the exhaust gases of the production of dilute nitric acid. Insofar as ammonia water cannot be evaporated in the 'hot' part of the bed, it was supplied into the central part of the catalyst bed (see Fig. 1 *c*).

The commercial application of this system showed that this way of ammonia feeding enhances the efficiency of this process above the theoretical estimates. Particularly, the gases were purified from nitrogen oxides to a very high extent and virtually no 'breakthrough' of ammonia was observed.†

The detailed kinetic studies of this process and its mathematical simulation [128–131] have shown that ammonia strongly

sorbs on the catalyst surface and reacts in its chemisorbed state with nitrogen oxides. In the reverse-flow process, ammonia sorbs in the exit part of the bed. Simultaneously, in its entry part, NO_x introduced with the intel gases react with ammonia sorbed in the previous cycle to form molecular nitrogen. After the flow reversal, this process is repeated. The adsorbed NH_3 is concentrated in the central part of the bed, which virtually totally prevents the loss of ammonia as a result of its desorption from the bed edges. The introduction of ammonia water into the middle part of the bed produces a positive side effect, namely, the direct contact between NH_3 and NO_x becomes possible only in the preheated parts of the reactor, which prevents the formation of explosive ammonium salts in the unit.

2. Deep oxidation of impurities volatile organic compound

Decontamination of exhaust gases of industrial plants from the impurities of volatile organic compounds (VOC), namely, hydrocarbons, alcohols, acids, ethers, esters, aldehydes, ketones, *etc*., is an important environmental problem.

If the exhausts contain high VOC concentrations, their decontamination may well involve the procedures of extraction and recycling of impurities, which are based on the absorption, adsorption, condensation and membrane processes.[31] For dilute gases, it is reasonable to use the thermal and catalytic oxidation of VOC with oxygen (usually, atmospheric oxygen) to harmless products, namely, carbon dioxide and water vapour; moreover, in the treatment of low-concentration exhausts, the catalytic reverse-flow processes that provide the autothermal (*i.e*., without additional supply of energy or fuel) processing of gases with the VOC content from 0.6 to 0.8 g m^{-3} and higher proved to be the method of choice from the economical and environmental viewpoints. Purification of gases with lower VOC contents requires additional energy to be supplied.

Thus, a pressing problem of the treatment of large volumes of vent gases with a very low concentration of harmful impurities (below 0.1 g m^{-3}) should be mentioned. This enhances the specific power consumption and increases the cost of decontamination systems. Moreover, such systems should be simple and safe in operation due to the abundance of exhaust sources at different kinds of plants and the quite probable lack of skilled staff.

The decontamination technologies that include the adsorption-catalytic processes meet the criteria mentioned. Their realisation usually requires a simple combination of adsorbers and catalytic reactors, *i.e*., VOC are first absorbed in a sorbent layer, which is followed by the sorbent regeneration (usually with water vapour or hot air) and the catalytic oxidation of impurities in a separate unit. However, in the framework of this review we are interested in adsorption-catalytic processes based on the VOC adsorption immediately on the surface of a deep-oxidation catalyst at low temperature with periodic regeneration of the catalyst by oxidation of sorbed impurities at elevated temperatures.[132–141]

Adsorption-catalytic processes exhibit substantial advantages over the conventional catalytic technologies of deep oxidation of VOC, especially in the processing of low-concentration gases. In this case, the use of such processes allows one to avoid permanent heating of gases to be cleaned, which reduces substantially power consumption. Their high technological flexibility makes it possible to decontaminate gases with the initial VOC concentration varying over a wide range and quickly put units into operation without preliminary heating. Such processes can be implemented within a one-reactor scheme (Fig. 5 *a*) with the periodic elevation of the temperature of the gas to be decontaminated at the reactor inlet in order to initiate the catalyst regeneration.

However, the practical experience and the results of mathematical simulation[142–145] revealed certain drawbacks of adsorption-catalytic processes. Thus partial desorption of non-oxidised VOC or the products of their incomplete oxidation is possible on heating of the catalyst, which reduces the degree of decontamination and necessitates additional purification of desorbed gases; there is also the risk of the reactor overheating during the regeneration.

These drawbacks can be overcome by the optimisation of flow schemes, operation conditions and parameters of the catalyst-adsorbent. Particularly, one of the ways to minimise desorption losses is the use of a procedure of stepwise heating of the catalyst during its regeneration.[136] In this version, the gradual heating in the beginning of the regeneration cycle allows one to transform a considerable part of weakly sorbed reactant into its strongly chemisorbed form. However, this approach is effective for a limited number of VOC and, moreover, substantially complicates the regeneration process and makes it more lengthy.

In addition, the losses can be reduced by using relatively coarse-grained catalysts-sorbents (*i.e*., by creating internal diffusion hindrances for the desorption).[146]

The reduction in the efficiency of decontamination due to the desorption of non-oxidised VOC can be avoided by using more sophisticated flow schemes that include, *e.g*., a post-reactor[134] (Fig. 5 *b*), which is preliminarily heated before the catalyst regeneration where final oxidation of the desorbed impurities occurs. Yet another version represents an adsorption-catalytic reverse process[142–144, 147, 148] (Fig. 5 *c*) where the adsorption phase involves the delivery of the original gases into

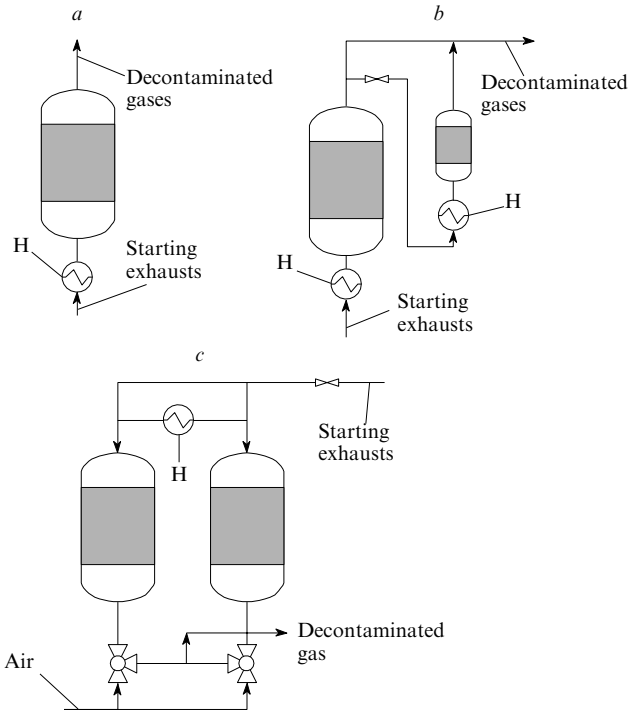


Figure 5. Flow schemes of adsorption-catalytic processes of deep oxidation of VOC.
(*a*) One-reactor scheme, (*b*) scheme with additional post-reactor, (*c*) adsorption-catalytic reverse process. From hereon, H is a heater.

† In other versions of the reverse process (*e.g*., with the ammonia delivery into the original mixture), the breakthrough caused by the ammonia desorption from the edges of the catalyst bed after the flow reversal posed a serious problem.[127]

two parallel reactors, and the regeneration occurs due to the heating of gases with simultaneous supply of air and periodic changes in the flow direction. In this case, VOC impurities are preferentially sorbed in the catalyst-bed parts adjacent to the point of inlet of the original gases, which allows one to minimise their losses in the desorption. Moreover, the efficient heat regeneration in the mode with the flow reversal makes it possible to considerably reduce the power consumed in the regeneration of the catalyst-sorbent.

It is of note that the developed model of adsorption-catalytic process allows one to cast a fresh glance on the conventional reverse process of deep oxidation of VOC (see Fig. 1 *b*). The results of simulation [149] have shown that at moderate temperatures in the inlet of the catalyst bed, before the flow reversal, the admixtures are adsorbed and a substantial part of them is sorbed reversibly. Alter the reversal of the flow, this part of the bed becomes the outlet and its temperature begins to increase. As a result, a part of sorbed substance can be sorbed to be flown away with the exit gas flow, which substantially decreases the overall degree of decontamination. To avoid this, it is necessary to use sufficiently long beds packed with an inert heat-regenerating material (the choice of this material is also important; in the ideal case, it should have the zero adsorption capacity with respect to VOC), and apply a reasonable strategy of the control over the process (particularly, it is important to choose the correct temperature of flow reversal at the catalyst – inert interface).

Of interest is a flowl scheme of an adsorption-catalytic process according to which the catalyst is regenerated by a combustion wave of sorbed VOC that moves towards the gas flow due to the heat conduction of the catalyst bed.[140, 145] A feature of this mode is that the desorbed substances get into the preheated part of the catalyst bed where they can be efficiently oxidised. However, according to mathematical simulations and experimental studies,[145] the motion of the coutercurrent heat front is possible only for the low linear filtration rates of the regenerating air. Under these conditions, it is possible to achieve complete conversion of oxygen present in the air flow and, as a consequence, the formation of partial oxidation products, including CO. It was proposed [145] to solve this problem by the installation of an additional post-reactor at the outlet main unit which substantially complicated the scheme and made it more expensive. At the same time, it cannot be ruled out that the use a catalyst-sorbent with a reduced adsorption capacity would be sufficient.

A process is known in which the catalyst regeneration and the oxidation of sorbed VOC occur upon simultaneous increase in the temperature and pressure in the closed space of the reactor-adsorber by delivery of compressed air.[150] The efficiency of this process is due to the fact that no flows at all exit before the end of regeneration and the VOC losses are impossible in principle. However, this process is technologically complicated and requires sufficiently high skill of the staff, which may limit its practical application.

An advantageous version of the adsorption-catalytic processes of VOC oxidation employs a spiral reactor (Fig. 6 *a*) consisting of two concentric metal spirals of which one is covered with a thin catalyst layer and the other is coated with a thin sorbent layer.[151] The original gas travels along one system of spiral channels to the spiral centre and then along the second system of channels from the centre to the exit. The gas is decontaminated by the adsorption. The periodic regeneration of the sorbent is performed by switching on a heater located in the centre of the spiral. The active heat exchange between the inlet and outlet gases provides the fast heating of the sorbent and the catalyst (due to the heat produced by the heater and

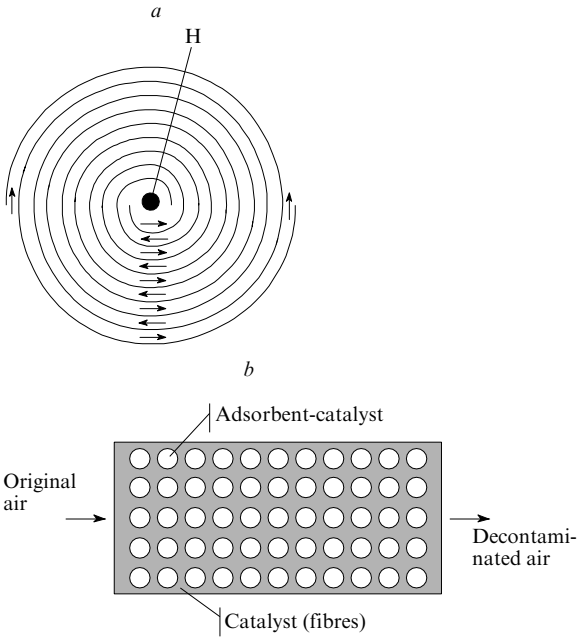


Figure 6. Promising schemes of adsorption-catalytic systems for decontamination of gases from VOC.
(*a*) Spiral adsorber-reactor, (*b*) multidispersed adsorption-catalytic system.

released in the VOC oxidation) with the minimum energy consumption. The high heating rate of the catalyst provides the high efficiency of oxidation of desorbed VOC to harmless products. Due to the complexity of spiral reactors, their practical implementation is hardly possible for high gas flow rates; however, they can be used in compact systems for local decontamination of air.

For the effective decontamination of gases from VOC, a multidispersed adsorption-catalytic system can be used [152] (Fig. 6 *b*), which consists of a relatively coarse-grain adsorbent-catalyst with the spaces between the grains filled with a microfibre catalyst. The typical geometric size of catalyst microfibres (< 10 μm) is substantially smaller that the grain size (> 1 mm); hence, the specific surface of fibres substantially exceeds that of grains. During the regeneration, the catalyst microfibres are heated in contact with the hot gas flow much more quickly than the grains of the catalyst-sorbent. Correspondingly, VOC desorbed during the regeneration phase come in contact with the preheated catalyst and are efficiently oxidised.

Returning to the second problem of adsorption-catalytic processes of deep oxidation, *i.e.*, the possible overheat of a catalyst above the threshold of its thermal stability, it should be noted that this problem might be solved by the optimisation of the maximum adsorption capacity of the sorbent-catalysts. For example, according to the results of simulations,[142, 144] this capacity should be from 1 to 2 mass % for the oxidation of aromatic hydrocarbons on the aluminium – chromium – copper catalyst (with the operation temperature limit of 750 °C).

In the development of adsorption-catalytic processes, attention was often focused on the elaboration and the use of catalysts and sorbents with the maximum possible adsorption capacity. However, in the general case, the optimum capacity for a process does not coincide with the maximum capacity of the catalyst.

3. Claus sulfur recovery process

The commercial production of elemental sulfur from acid waste gases of certain industrial processes is based on the Claus reaction

$$H_2S + \frac{1}{2}SO_2 \rightleftharpoons \frac{1.5}{n}S_n + H_2O. \quad (2)$$

This reaction is reversible and exothermic; hence the maximum degree of sulfur recovery from gases is, as a rule, limited by thermodynamic parameters. The catalytic process usually involves several stages. Between the stages, the gases are cooled and the sulfur formed is removed. However, even this does not help in reaching the required degree of sulfur recovery.
Obviously, the equilibrium in the Claus reaction can be shifted to the products upon removal of one component of the gas mixture (sulfur or water) directly in the course of reaction.

a. Sulfur condensation and adsorption

According to one version, the Claus reaction is carried out at a temperature below the dew point of sulfur vapour and its condensation occurs directly in the catalyst bed. The transfer of sulfur from the gas to the condensed state can substantially shift equilibrium (2), although this requires the timely cleaning of the catalyst from liquid sulfur by its evaporation. The basics of this approach were formulated by Claus back in the 19th century.[1,2] Later, the concept of Cold Bed Adsorption was formulated, which gave rise to the development of the commercial CBA [153] and Sulfreen[154] processes, which are widely used in the modern industrial practice of Claus units tail gas cleanup and make it possible to increase the total degree of sulfur recovery from 96% – 98% (the theoretical limit for two- and three-stage stationary Claus units) to 99.5% and higher. For the comprehensive review and the analysis of these technologies, see Ref. 155. It should be noted that sulfur vapour is removed from the gas mixture by both their condensation and the adsorption in the catalyst pores; therefore, the use of the term 'adsorption-catalytic' process is justified in this case.

The realisation of such processes requires the use of multireactor parallel schemes (see Fig. 3 *b*) containing, as a rule, two or three reactors in which, in turn, the following stages alternate: reaction/surfur adsorption, catalyst regeneration (evaporation of sulfur at elevated temperature of the catalyst in a flow of a hydrogen sulfide-containing gas) and reactor cooling.

Moreover, schemes are known in which the catalyst regeneration and the removal of sulfur are carried out using the hot reaction gas delivered from the Claus furnace; as an example, a process [156] in which the unsteady-state conditions in three successive catalyst beds are realised by the periodic shift of the position of the inlet and outlet points of the reaction mixture and, correspondingly, by the change in the succession of catalyst beds the gas flow passes through. Conceptually, this scheme is close to the 'torus' scheme (see Fig. 2 *a*) and also to a scheme with the pseudomoving catalyst beds (see Fig. 4). According to the results of modelling, such a scheme allows up to 99.9% of sulfur to be recovered; moreover, whereas the aforementioned conventional technologies such as Sulfreen serve only for the cleanup of tail gases from stationary Claus units, the proposed scheme is an alternative for the complete combination of the Claus and Sulfreen methods (with virtually the same capital and operational costs as in the Sulfreen process).

b. The Claus reverse processes

Yet another version of processes that include sulfur condensation and evaporation is the Claus reverse process,[157 – 165] which due to the periodic reversal of the flow, allows one to carry out the reaction at a low inlet gas temperature, *i.e.*, under the conditions of sufur condensation.

Mathematical models of this process have shown[161 – 164] that under these conditions, a zone with a temperature above the sulfur dew point is formed in the central part of the catalyst bed. In this zone, the Claus reaction occurs, while in the cooler edge zones, sulfur is condensed and evaporated. In the reverse process, the maximum temperature in the reaction zone that defines the equilibrium yield of sulfur can exceed the sulfur dew point merely by several degrees; as a result, this temperature is substantially lower as compared with the stationary process (the maximum temperature of the latter is determined by both the dew point as the minimum inlet gas temperature and the adiabatic heat of the Claus reaction). This allows one to reach higher degrees of conversion of the starting reactants.

Particularly, the one-stage Claus reverse process, which is carried out by the schemes shown in Fig. 1 *a*,*b*, is equivalent to the two-stage stationary process as regards the total degree of sulfur recovery (up to 96%), whereas the reverse process with intermediate heat removal [159] (see Fig. 1 *c*) is equivalent to the conventional three-stage process with the degree of sulfur recovery approaching 98%. Moreover, the reverse process does not require heat exchangers and the preliminary heating of gases, which makes this technology substantially cheaper.

The one-stage reverse process has the following drawbacks: the degree of sulfur recovery is $< 96\%$; a part of sulfur is lost as a result of the incomplete hydrolysis of CS_2 and COS usually present in the reaction gas; sulfur is lost due to the formation of a fog from its vapour. These disadvantages can be overcome by using the Claus 'double' reverse process [160] (Fig. 7). The unit includes three reactors, of which the first operates at high temperature of the gas delivered from the Claus furnace (300 – 400 °C), while the second and third reactors operate at temperatures below the sulfur dew point (120 – 160 °C). Continuous operation of the second reactor is provided by periodic reversals of the gas flow in the internal circuit, while the catalyst regeneration in the third bed occurs when the order of reactors the gas passes through is changed upon the reversal of the flow direction in the external circuit. High temperature in the first (with respect to the gas flow) reactor favours the efficient hydrolysis of CS_2 and COS and also the efficient regeneration of the catalyst (due to the evaporation of liquid sulfur accumulated in the previous phase of the external cycle). The high overall degree of conversion and also the condensation and adsorption of non-condensed sulfur vapour are

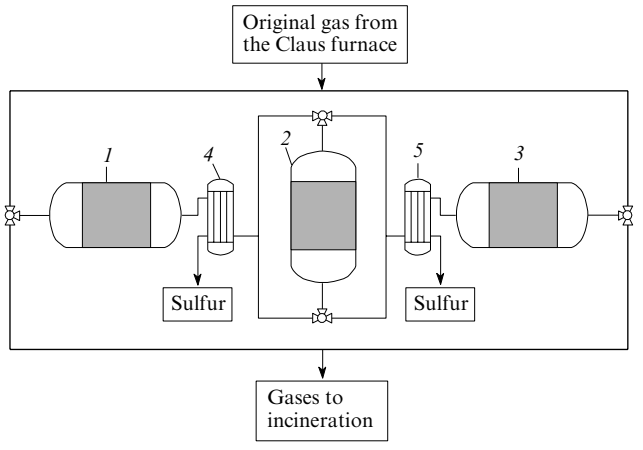


Figure 7. Flow scheme of the Claus 'double' reverse process. (*1* – *3*) Catalytic reactors, (*4*, *5*) units for sulfur condensation.

favoured by the low temperature in the third reactor (with respect to the gas flow).

According to the results of modelling,[164] the 'double' reverse process provides a high degree of mixture conversion, efficient hydrolysis of COS and CS_2 and elimination of sulfur losses with non-condensed fog (the total level of sulfur extraction was 99.6% – 99.8%). This process is advantageous due to the absence of strict requirements to the quick response of switching valves. This is associated with the fact that the switches in the external cycle are rare (about once in a day) and the losses in the switch are insignificant, while the gas breakthroughs in the switches in the internal circle (the characteristic switch frequency is several times per hour) is damped by the protective action of the third bed. The units for the 'double' reverse process do not require complex equipment and thus are very compact.

Pilot-plant tests of the Claus reverse process [165] confirmed its feasibility.

c. Adsorption of water vapour

As was noted above, the equilibrium in the Claus reaction can be shifted by the removal of water vapour from the reaction mixture. The Claus process in a combined bed containing catalyst grains and a zeolite sorbent was described. [166–169] The scheme of this version provides for a two-stage reverse process (see Fig. 1 *c*) with the intermediate heat exchange and the intermediate sulfur removal. The original gas is fed to the reactor at a temperature that exceeds the dew point of sulfur vapour (*e.g.*, at 250 °C). In the first bed, the Claus reaction and the adsorption of water vapour on the sorbent (zeolite) occur simultaneously. The gases that exit from the second bed are first cooled for sulfur condensation and then heated to higher temperature before entering the second bed where the water vapour is desorbed. As the sorbent is saturated with water, the flows in the first bed are reversed and the process is carried out in the same mode.

According to theoretical and experimental studies,[166–169] removal of water vapour by adsorption provides a substantial shift of the reaction equilibrium and ensures virtually 100% conversion of the mixture even for high initial contents of reactants and the cycle time between reversals of no less than 1 h. However, it was noted [169] that such a scheme has certain drawbacks, particularly, it does not rule out a decrease in the efficiency of the hydrolysis of COS, which may be present in the gases. At the same time, they assumed that these drawbacks can presumably be minimised or eliminated provided the optimum combination of the time-dependent concentration and temperature fields in the catalyst beds will be found.

4. Low-temperature decomposition of hydrogen sulfide

Direct decomposition of H_2S is one of the methods for the production of elemental sulfur from hydrogen sulfide

$$H_2S \rightleftharpoons H_2 + \frac{1}{n}S_n. \qquad (3)$$

This method attracts attention due to the possibility of the production of hydrogen (in place of water in the Claus process) in addition to sulfur, which is important in view of the development of hydrogen energetics.

However, all attempts to develop a commercial process of decomposition of hydrogen sulfide faced serious thermodynamic limitations, namely, reaction (3) is reversible and the equilibrium degree of hydrogen sulfide dissociation is virtually zero under ordinary conditions. To achieve the equilibrium H_2S conversion of about 10%, the temperature should be elevated to 700 °C, while its complete dissociation requires temperatures of nearly 2000 °C. It is difficult to carry out such a process; moreover, recombination of sulfur and hydrogen to H_2S during the cooling of the reaction products is probable, and the elimination of this route would require additional efforts.

In the industry, acidic gases producted upon refining of natural gas and oil and containing, as a rule, considerable amounts of hydrocarbons and carbon oxides in addition to H_2S are the main source of hydrogen sulfide. At high temperatures, there is a high probability for the pyrolysis of these compounds, which may substantially complicate the technology, *viz.*, necessitate the use of rather intricate and expensive equipment for the separation and purification of H_2S before its utilisation.

The use of the adsorption-catalytic process proved to be an effective (and interesting within the framework of this review) way for overcoming the equilibrium limitations of the degree of dissociation of hydrogen sulfide and also for the decrease in the reaction temperature.

The known methods of H_2S decomposition [170–172] involve hydrogen sulfide chemisorption on the surface of sulfides of transition metals (iron, nickel, cobalt, copper, *etc.*), which is accompanied by the formation of surface polysulfides of metals and hydrogen, and periodic thermolysis of polysulfides to the original sulfides and sulfur. Chemisorption proceeds at relatively low temperatures (200 – 550 °C), which, nonetheless, allows one to achieve high degrees of H_2S decomposition. The sorbent is regenerated by heating to 700 – 800 °C in a gas flow containing no hydrogen or hydrogen sulfide, which results in the release of elemental sulfur.

Startsev *et al.*[173–176] have shown experimentally that the stage of hydrogen sulfide chemisorption can proceed at a sufficiently high rate even at room temperature, whereas the regeneration occurs at temperatures not exceeding 200 – 300 °C provided the supported sulfide catalysts or certain catalytically active systems are taken as the chemisorbents.

Figure 8 shows the dynamics of hydrogen evolution in the stage of hydrogen sulfide chemisorption where the gas mixture is fed to the sulfide catalyst bed. In the beginning of the experiment, almost 100% adsorption of hydrogen sulfide was observed; moreover, even at room temperature, considerable amount of hydrogen evolved. If relatively short cycles (< 10 min) were used, the process involved no discharge of hydrogen sulfide into the gas phase and the degree of H_2S decomposition was 100%. Periodic regeneration of the catalyst-chemisorbent at moderate temperatures (200 °C) allowed complete recovery of its chemisorption properties. This was confirmed in multiple chemisorption – regeneration cycles.

At the first glance, the possibility of achievement of that high degree of hydrogen sulfide decomposition to sulfur and

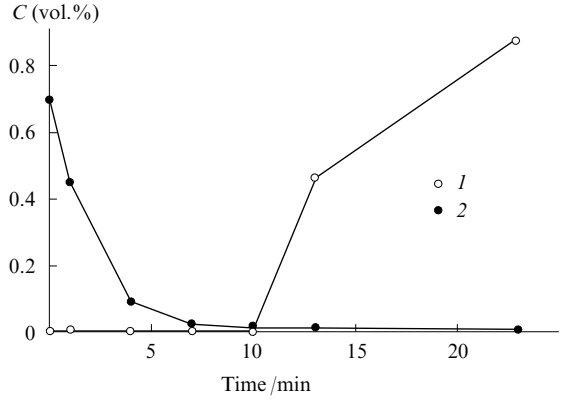


Figure 8. Time changes in the outlet concentrations of H_2S (*1*) and H_2 (*2*) at the feeding of a gas mixture containing 1 vol.% H_2S to the sulfide catalyst bed.
T = 20 °C, P = 1 atm, contact time is 1 s.

hydrogen at low temperatures contradicts the thermodynamic limitations. This is rationalised as being due to different states of a catalyst in a periodic adsorption-catalytic process, which enables the spatial and temporal separation of the reaction stages and allows one to substantially shift the equilibria.

In the general case, the sequence of stages is as follows:

$$MS + x\,H_2S \rightleftharpoons MS_{x+1} + x\,H_2, \quad (4)$$

$$MS_{x+1} \rightleftharpoons MS + \frac{x}{n}S_n. \quad (5)$$

A simplified scheme includes the transformation of iron sulfide into disulfide in the chemisorption stage

$$FeS + H_2S \rightleftharpoons FeS_2 + H_2 \quad (6)$$

and the reverse transformation in the regeneration stage [143]

$$FeS_2 \rightleftharpoons FeS + \frac{1}{n}S_n. \quad (7)$$

Figure 9 shows the equilibrium degrees of conversion of sulfides according to reactions (6) and (7). Reaction (6) is exothermic and virtually irreversible in the low-temperature range. Decomposition of FeS_2 to sulfur proceeds with the absorption of a large amount of heat [which ensures the total endothermic effect in the overall reaction (3)] and is thermodynamically less advantageous (which explains the low equilibrium degree of H_2S dissociation under steady-state conditions at low temperatures).

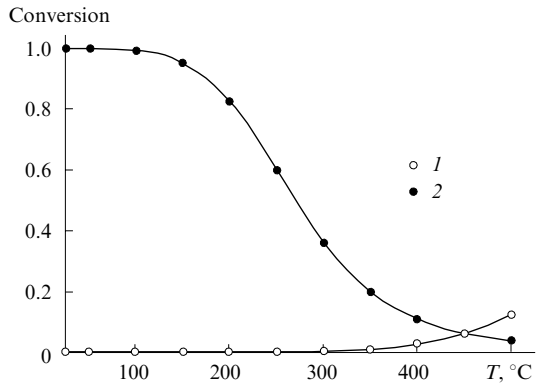


Figure 9. Equilibrium degrees of conversion of sulfides according to the reactions (7) (*1*) and (6) (*2*).

However, the equilibrium degree of sulfide dissociation concerns only steady-state modes of reactions and imposes no direct limitations on the operation of a flow-through reactor with the variable catalyst state. Continuous removal of sulfur vapour from the reaction zone with a flow of a regenerating gas gradually enables complete regeneration of the chemisorbent-catalyst surface. Under these conditions, the equilibrium degree of dissociation determines the regeneration time rather than its maximum degree. It is of fundamental significance that the regeneration occurs in the absence of hydrogen in the gas flow, which eliminates the reverse process, *i.e.*, the H_2S formation.

Obviously, the above description is quite simplified. A much more comprehensive study with involvement of the quantum chemical simulation [176] has shown that the formation of complex compounds comprising hydrogen atoms in addition to the metal and sulfur occurs in the chemisorption of hydrogen sulfide on the surface of a sulfide catalyst.

It should be emphasised that the attainment of super-equilibrium degrees of H_2S dissociation is only possible in a periodic chemisorption-catalytic process with the well-defined separation of the chemisorption and regeneration stages in space and time

The low-temperature decomposition of hydrogen sulfide can be carried out in a multireactor system (see Fig. 3 *b*) with the periodically alternating delivery of a cold gas containing hydrogen sulfide and a heated regeneration gas (*e.g.*, commercial nitrogen, carbon dioxide, natural gas, *etc.*) to each reactor. Such a technology allows one to achieve the 100% conversion of hydrogen sulfide at quite moderate temperatures. At low temperatures, the requirements to construction materials and to the heat removal from the reactor become less severe, in addition, complex sour gases containing hydrogen sulfide can be processed without preliminary extraction and purification of H_2S. Moreover, this reduces the energy consumption due to not only the minimisation of the heat loss as a result of the lower operation temperatures, but also the substantial shift of the heat balance of this reaction. Thus at $T > 600$ °C, the endothermic effect of the sulfur formation as the molecules S_2 was 90 kJ mol^{-1}, while at $T \sim 200$ °C, where S_6 and S_8 are the dominant allotropic forms of sulfur, the effect decreased to 35–40 kJ mol^{-1}. This decrease was caused by strongly exothermic reactions of sulfur molecule growth in the series $S_2 \rightarrow S_6 \rightarrow S_8$.

The chemisorption-catalytic processes are advantageous in a situation where the volume of produced hydrogen is of importance. Particularly, their use is promising in the processing of sour natural gases, *e.g.*, the gas from the Astrakhan gas field, which contains 30% H_2S. The obtained hydrogen can be utilised in fuel cells for the electric power production.

5. Oxidation of sulfur dioxide

Sulfur dioxide oxidation

$$SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$$

is a reversible reaction the equilibrium in which can be shifted by adsorption effects. There are two adsorption-catalytic approaches that can substantially enhance the efficiency of the conventional version of this reaction.

a. Water flushing of the catalyst

The first way of shifting the reaction equilibrium is the oxidation of sulfur dioxide at low temperatures in the presence of water vapour. Under such conditions, sulfur trioxide reacts with water to form a sulfuric acid condensate, thus shifting the equilibrium of the target reaction.

The processes of SO_2 oxidation at 35–80 °C on activated carbon (this catalyst was chosen because the conventional vanadium catalysts are inactive at low temperatures) with the initial concentrations of sulfur dioxide of 0.1 vol.%–0.5 vol.% were studied.[177–179] Under these conditions, the acid formed was condensed and sorbed in the catalyst pores. The catalyst was regenerated by flushing it with water.

The described processes, which were characterised by rather lengthy operation cycles, namely, up to 100–200 min, made it possible to reach very high degrees of sulfur dioxide conversion (the residual concentration of SO_2 in gases was about 50 ppm). However, the use of water flushing leads to the formation of vast amounts of off-grade (low-concentration) acid, which substantially limits the practical application of this technology.

b. Flushing of catalyst beds with air

Yet another method aimed at the shift of the equilibrium to enhance the efficiency of SO_2 oxidation takes advantage of the

adsorption properties of the molten active component of conventional vanadium catalysts.

It was shown [180] that the alternating feeding of the reaction mixture and air to the vanadium catalyst bed can substantially increase the degree of sulfur dioxide conversion. Presumably, flushing of the catalyst bed with air leads to the supersaturation of a film of the molten active component on the catalyst surface with oxygen so that in the next reactant feeding cycle, the oxygen concentration in the melt substantially exceeds its equilibrium value (with respect to the reaction mixture composition); and, hence, the degree of SO_2 conversion can also exceed the equilibrium limit reached in the steady-state mode.

This process can be implemented in a two-reactor scheme (see Fig. 3 *b*) with separate delivery of air and the reaction mixture according to two main versions, namely, with direct flow [180] and counter flow.[181] The calculations [182] carried out within the framework of a one-dimensional model of an adiabatic catalyst bed that operates under the plug flow conditions[183] together with a comprehensive unsteady-state kinetic model of this process, [184] have shown that both versions allow one to reach extremely high degrees of SO_2 conversion (> 99.9%). However, the counterflow version provides stable operation of the system in much wider ranges of initial concentrations of sulfur dioxide and inlet gas temperatures and, hence, can be carried out at technologically favourable parameters (cycle duration, catalyst load, initial temperature of gases, *etc*.) in the second stage of the sulfuric acid contacting schemes DC/DA (double contacting/double adsorption). In this case, the total degree of sulfur dioxide conversion in the contact unit can reach 99.999%, which corresponds to the final SO_2 concentration on a level of 50 ppm and meets the most severe environmental requirements. These theoretical conclusions were successfully confirmed by the pilot tests.[143]

6. Steam reforming of methane and CO

The reforming of methane and other hydrocarbons aimed at the production of hydrogen, which is utilised in the syntheses of ammonia and methanol and in the petroleum industry and hydrogen energetics, is among the most important directions of chemical technology.

In these technologies, the most important stages are the methane steam reforming

$$CH_4 + H_2O \rightleftharpoons CO + 3\,H_2$$

and the CO steam reforming (water gas shift-reaction)

$$CO + H_2O \rightleftharpoons CO_2 + H_2\,.$$

In both cases, the formation of hydrogen is limited by the equilibrium factors. According to the thermodynamic analysis, the hydrogen yield can be substantially increased if carbon dioxide is removed from the reaction zone. The removal of CO_2 can be accomplished by its adsorption, particularly, on metal oxides, to form carbonates.

Attention is focused on the reaction of methane steam reforming, the equilibrium of which can be shifted due to the absorption of carbon dioxide [185–193] by various sorbents (CO, MgO, hydrotalcite, dolomite, lithium zirconate, *etc*.). In a single-stage process, hydrogen with the purity grade from 85% to 98% is produced; moreover, the residual mixture mainly contains methane with the minimum amounts of carbon oxides.

Analogous studies have also confirmed the possibility of a substantial shift of the chemical equilibrium in water gas shift reaction by the adsorption of CO_2 on CaO.[194] In this case, hydrogen with the purity grade of 99.5% was formed.

The reverse reaction, namely, the carbon dioxide reduction with hydrogen to CO and water, also deserves mention.[195] In this case, the virtually 100% CO yield was reached due to the adsorption of water on a zeolite sorbent.

It should be stressed that the developments mentioned above were based on a concept of the catalyst steady state, whereas the non-stationarity of the process was entirely attributed to the sorbent effect. Particularly, the well-known steady-state model[196] was used in the simulation of the processes of methane steam reforming. However, the correctness of this approach was not substantiated and is not self-evident.

An interesting scheme was proposed,[197] in which cyclic feeding alternation of steam and the synthesis gas was used in the production of hydrogen on an iron oxide catalyst

$$3\,FeO + H_2O \longrightarrow Fe_3O_4 + H_2\,,$$

$$Fe_3O_4 + CO \longrightarrow 3\,FeO + CO_2\,.$$

This process, which was named the Reformer Sponge Iron Cycle (RESC), can be employed in the production of hydrogen from the natural gas, liquid hydrocarbon fuels and coal gasification products. Similar schemes were proposed recently.[198, 199]

The production of hydrogen by the catalytic pyrolysis of hydrocarbons with the simultaneous production of valuable types of activated coal is actively developed.[200–209] In this method, carbon is deposited and accumulated on the catalyst surface, and the processes involved are basically unsteady.

7. Anaerobic oxidation of methane

At present, the processes of cyclic oxidation of methane under anaerobic conditions, where nickel and iron oxides are used as the catalysts, are actively studied. [210–213] These processes are called Chemical-Looping Combustion (CLC). They are aimed at the deep oxidation, which is achieved by the correct choice of the reaction temperature (1000 °C) and the catalyst composition. Natural gas is passed through a catalyst bed to oxidise hydrocarbons to CO_2 and water vapour; the catalyst is periodically reoxidised with air.

This processes is meant particularly for energy purposes, *e.g*., for the electric power production. What is its main advantage over the conventional combustion of natural gas consists, is that in the hydrocarbon delivery cycle, the gas mixture at the outlet from the reactor contains only carbon dioxide and water vapour. Due to relative simplicity of water removal from this flow, highly concentrated CO_2 can be produced and extracted later in the pure form and utilised without its emission to the atmosphere. The latter factor is currently the topical problem in view of the Kyoto Protocol requirements. The second advantage of this process is the relatively low temperature in both phases of the cycle, which allows substantial reduction of the emission of nitrogen oxides to the atmosphere.

8. Anaerobic processes of oxidative dehydrogenation of hydrocarbons

The quest for the ways of increasing the selectivity of target reactions in complex reaction systems is among the currently topical problems of catalysis. These reactions include numerous processes of selective catalytic oxidation of hydrocarbons (propane to propylene, butane to butylene and butadiene, *etc*.).

As was shown above, the way of enhancing the selectivity of conversion and the yield of target products as compared with steady-state processes lies in the use of the unsteady state of a catalyst, which can be generated by the cyclic separate feeding of hydrocarbons and the oxidant (air). Oxygen chemisorbed on the catalyst surface acts as the oxidant, whereas

molecular oxygen is not present in the hydrocarbon flow (this explains the term 'anaerobic process').

Reactions of selective oxidation of hydrocarbons with oxygen are, as a rule, exothermic and the selectivity of most of them decreases as the temperature increases. As a consequence, the maximum concentrations of reactants are limited in a steady-state adiabatic process, which has a negative effect on the efficiency. Apparently, the effective coupling of heat and concentration fronts in the catalyst bed is the key problem in the elaboration of selective oxidation processes.

Model studies of parallel adiabatic endothermic reactions have shown [143, 214–216] that under adiabatic conditions the cyclic feeding of a preheated hydrocarbon into a cold bed of a preliminarily oxidised catalyst leads to substantially lower maximum temperatures as compared with the steady-state process. This is associated with the fact that, in the former case, a considerable portion of heat released in oxidation reactions is consumed for the catalyst heating. The lower temperatures, in turn, favour the higher reaction selectivity. Moreover, this allows one to feed concentrated hydrocarbons into the reactor, which makes it possible to substantially enhance the efficiency of the process.

Model studies also showed the possibility of the existence of a reversed heat front, which, due to the heat conduction of the bed, can move in the catalyst bed counter-currently the reaction gas flow. This allows one to additionally decrease the maximum temperature and enhance the oxidation selectivity.

In the studies [142, 217] devoted to the processes of selective oxidation of hydrocarbons with the separate delivery of reactants, propane oxidative dehydrogenation to propylene on a vanadium-oxide catalyst was considered. The system of reactions can be written as follows:[104]

$$C_3H_8 + [V_2O_5] \longrightarrow C_3H_6 + H_2O + [V_2O_4], \quad (8)$$

$$C_3H_6 + 9[V_2O_5] \longrightarrow 3CO_2 + 3H_2O + 9[V_2O_4], \quad (9)$$

$$C_3H_8 + 10[V_2O_5] \longrightarrow 3CO_2 + 4H_2O + 10[V_2O_4], \quad (10)$$

$$[V_2O_4] + \frac{1}{2}O_2 \longrightarrow [V_2O_5]. \quad (11)$$

According to rough estimates, the stage of selective oxidation (8) produces a virtually zero (within the calculation error) heat (about -4.6 kJ per mole of propane), while the total exothermic effect of the overall selective oxidation of propane (116.8 kJ mol^{-1}) is largely due to a sufficiently high exothemic effect in the catalyst reoxidation stage (11), namely, 121.4 kJ per mole of V_2O_4. At the same time, the stages of deep oxidation of propylene (9) and propane (10) are characterised by pronounced heat evolution (840 kJ mol^{-1}) approximately the same for both these reactions.

Based on these results, a very important conclusion can be drawn, *viz*., the temperature conditions of the process depend not only on the catalyst activity and selectivity, but also on its thermodynamic properties, particularly, the energy of the bond between chemisorbed oxygen and the surface, which determines the redistribution of the released heat between the stages of catalyst reduction (8)–(10) and reoxidation (11).

According to model studies,[217] feeding of pure propane with a temperature of 300 °C into a cold bed of a preliminarily oxidised catalyst gives rise to a thermal front that travels toward the filtrating gas flow. In the front, due to the virtually zero thermal effect of the main reaction and the insignificant extent of deep oxidation reactions, the catalyst is not heated above the outlet gas temperature.

In addition, such a process can be carried out in a continuous mode with a cyclic separate feeding of cold propane and air in counterflows, *e.g*., according to the two-reactor scheme (see Fig. 3 *b*), into the preliminarily heated catalyst bed. As a result, a stable autothermal unsteady mode is generated in this bed (Fig. 10), which eliminates the necessity of the energy supply and the preheating of reaction flows.

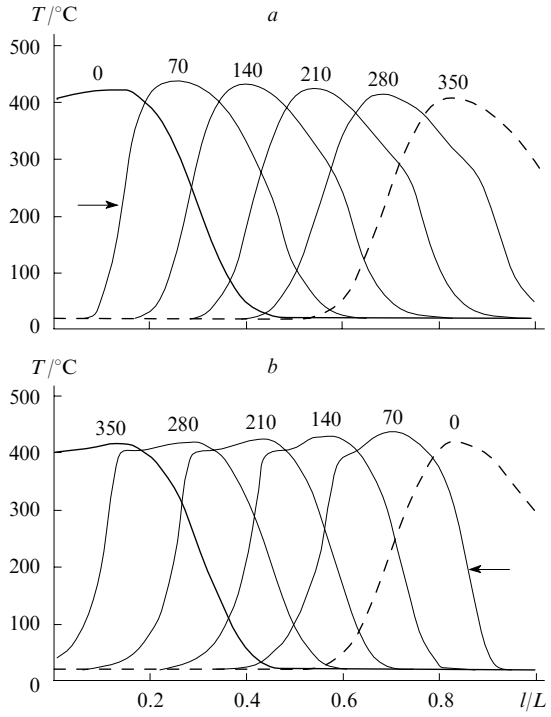


Figure 10. Temperature profiles of a catalyst along the bad length in the established cyclic mode with separate counter-current feeding of propane and air.
(*a*) Propane feeding cycle (catalyst reduction), (*b*) air feeding cycle (catalyst reoxidation). Arrows show the direction of the reaction mixture flow, numbers over the curves show time (in s) from the beginning of each cycle. The inlet gas temperature was 20 °C in both cycles, the cycle duration was 350 s.

According to estimates, the use of concentrated propane makes it possible to increase the efficiency as compared with steady-state technologies and also noticeably enhance the selectivity of propane oxidation. Among the other advantages of this process, the following factors deserve mention.

1. Technological simplicity and low costs required for its implementation, which is associated with the use of simple and inexpensive reactors with steady-state adiabatic beds of catalyst grains and with the minimum use of the heat-exchange infrastructure.

2. Safety of the process, which is due to the absence of direct contact between hydrocarbons and oxygen.

3. A possibility of utilising air as the oxidant in place of pure oxygen.

4. The possibility of prolongation of the catalyst service life due to the effective suppression of the coke formation in the stage of propane conversion (as a consequence of low temperatures) and to the burning out of coke with oxygen in each cycle of catalyst reoxidation

The processes under consideration also include the dehydrogenation of paraffins to alkenes, which involves the selective anaerobic oxidation of hydrogen over transition metal oxides and periodic reoxidation of the latter with air,[218, 219] the partial oxidation of n-butane to maleic anhydride [220] (implemented on the commercial scale by DuPont company) and of *o*-xylene to phthalic anhydride [221] in moving catalyst beds and also the oxidation of paraffins to alkenes [222] with separate feeding of hydrocarbons and oxygen.

9. Purification of automotive exhaust

The currently topical problems include the problem of 'cold start', which concerns the idle start of an engine when the catalyst temperature is too low.

A solution to this problem lies in the corporation of adsorption traps into the catalytic neutralisers. These traps can adsorb toxic impurities (CO, hydrocarbons, NO_x) and soot particles from the exhaust gases.[223–226] However, although the sorbed hydrocarbons and soot can be oxidised to the higher or lesser extent, removal of nitrogen oxides poses certain difficulties associated with the fact that these oxides are desorbed during heating of the neutraliser much sooner than the temperature necessary for their efficient reduction is reached.

An original solution to this problem was patented.[227] In essence, the patent describes a procedure for the reversal of flows in a multibed system inert–catalyst–sorbent–catalyst–inert, where the reversal is carried out by a mechanical rotationt of this system.

At a low temperature, the impurities are accumulated in the sorbent located between two catalyst beds. As the temperature increases, the catalyst beds are first to be heated, while the sorbent layer is heated later. Thus, the desorption of impurities begins only when the catalyst temperature becomes sufficient for its effective decontamination. This process may be a good illustration of the effective interrelation between the adsorption properties of the system and the dynamics of thermal fields in it.

10. Miscellaneous processes

Among the other processes actively employing the sorption properties of catalysts, the following processes can be singled out:

— direct synthesis of HCN from CO and ammonia with sorption of CO_2 formed on lithium zirconate;[166]

— the unsteady Deacon process [228, 229] of complete oxidation of HCl to elemental chlorine, which includes separate stages, namely, chemisorption of hydrogen chloride on copper oxide to form $CuCl_2$ and water vapour and the regeneration of the sorbent due to the copper chloride oxidation to form CuO and Cl_2;

— a cyclic process of alkene synthesis from methane through transient bromination of methane, which includes the stages of chemisorption of molecular HBr on oxide sorbents used in this process and periodic regeneration of the sorbent to form elemental bromine;[230]

— synthesis of methanol with removal of the product formed by its absorption with a fine-grain sorbent continuously filtered through a fixed catalyst bed;[231]

— dehydrogenation of cyclohexane to benzene over a metal-hydride catalyst with chemisorption removal of hydrogen;[232]

— unsteady processes of hydrodesulfurisation and hydrodearomatisation of fuels, which take advantage of high adsorption capacity of the catalyst with respect to sulfur compounds [233, 234] and include reverse processes for hydrotreatment.

All the processes listed above are based on the sorption properties of the catalytic surface and could be carried out in unsteady-state modes with the efficiency enhanced as compared with steady-state processes and particularly afforded superequilibrium yields of the reaction products.

IV. Conclusion

The studies of sorption-catalytic processes described above showed that the purposeful use of sorption (adsorption and chemisorption) properties of heterogeneous catalysts allows one to substantially enhance the efficiency of many catalytic reactions. The highest technological effect can be achieved for a controlled combination of the thermal non-stationarity with the composition non-stationarity of the catalyst surface.

In the elaboration of a new process, when choosing the main active factor (*e.g.*, concentration modulation), it is necessary to take into account the other factors (dynamic changes in the temperature and the pressure). Otherwise, instead of the expected improvement in the characteristics as compared with steady-state processes, one may obtain a zero and even negative effect.

It should be borne in mind that unsteady catalytic processes are cyclic or periodic, and certain technological efforts may be necessary to ensure their recurrence and, in most cases, the uninterrupted operation of the system as a whole. This complicates practical implementation of such technologies and makes them less attractive; hence, their development is reasonable only if the unsteady-state mode offers substantial advantages over the steady-state processes. Correspondingly, this entails high requirements to the skill of developers and the quality of their service, while the success is determined by the deep insight into the phenomena observed and the use of modern experimental techniques and the methods of comprehensive mathematical simulation.

The diversity of methods for the development of unsteady-state conditions and their combinations is even reflected in the yet unsettled terminology used in the literature. The term 'unsteady catalysis' is often used, although it is too wide and, in certain cases, ambiguous. Insofar as the technologies with modulating catalyst state actively utilise the adsorption phenomena, the term 'sorption-enhanced catalytic processes' is often used. Other popular terms are 'multifunctional processes', which reflects simultaneous occurrence of different types of phenomena (*e.g.*, adsorption and catalysis), and 'chemical looping', which characterises the cyclic nature of processes. The latter are sometimes called (however, not always correctly) the 'reactive chromatographic' processes.

The development of unsteady and adsorption-catalytic processes is a very sophisticated task, which requires that a large number of different factors and their combined action on different-scale levels of the process be understood and taken into account. It should be noted that many relationships typical of steady-state processes do not in principle valid the unsteady catalytic processes.

Particularly, in unsteady processes, even in formally adiabatic catalyst beds, the conditions are realised where the temperature in the bed substantially deviates from the adiabatic value. This difference is determined, in addition to the dynamic effects associated with the regenerative heat exchange and the motion of thermal fronts in the catalyst bed (a property typical of conventional reverse processes with the thermal non-stationarity of the catalyst), by the possible dynamic redistribution of released heat, which occurs in different reaction stages and phases, in both space and time (this is a unique property of systems with the sorption non-stationarity). Depending on the chosen strategy of the realisation of the unsteady mode, the maximum temperature in the process can be either substantially lower (*e.g.*, as in the anaerobic oxidation of hydrocarbons, see Section III.8) or higher (as in the adsorption-catalytic process of VOC oxidation, see Section III.2) than the adiabatic temperature in an equivalent steady-state process.

The use of the sorption capacity of the catalyst allows one to carry out individual reaction stages within certain phases of the technological cycle, which opens up wide prospects for the modulation of the reactant concentrations on the catalyst surface. In many cases, the correct organisation of this process in combination with the temperature factor allows one to overcome the equilibrium limitations and reach higher yields of the target products as compared with analogous steady-state processes.

It is of note that in many cases the parameters of unsteady modes substantially depend on the factors that play a minor role or have an indirect effect on the steady-state technologies. These factors include the bond energy of the reactant with the catalyst surface, the heat capacity of the catalyst, its specific surface, *etc*.

Summarising, the following advantages of the sorption-catalytic technologies over the steady-state methods can be mentioned:

— a decrease in the energy consumption in the processing of low-concentration gases (deep oxidation of VOC);

— an increase in the efficiency of decontamination of exhaust gases (NO_x reduction and purification of automotive exhausts);

— superequilibrium yields of target products in thermodynamically limited reactions (the Claus process, H_2S decomposition, SO_2 oxidation, steam reforming of methane and CO, the Deacon process, *etc*.);

— the enhanced selectivity of partial oxidation processes provided by the use of chemisorbed oxygen as a 'soft' oxidant (oxidation of n-butane to maleic anhydride, *o*-xylene to phthalic anhydride, paraffins to alkenes, *etc*.).

In many cases, these advantages may include the reduction in the capital costs in the realisation of these processes and also, paradoxical as this may look at the first glance, the simplification of flow schemes and the enhancement of their operation stability.

However, it should be stressed that the aforementioned improvements are achieved only in the case of optimally organised processes. Otherwise, the utilisation of catalyst sorption properties may have a negative effect. Particularly, as was demonstrated above by the example of reactions of deep oxidation of VOC and of the reduction of nitrogen oxides and the oxidation of sulfur dioxide, the sorption – desorption phenomena in a conventional reverse process reduce its efficiency; and, hence, different technological approaches are required in order to achieve positive effects. This is why the key factor of the successful development of sorption-catalytic processes is the correct choice of the process scheme and the search for the optimum strategy for its dynamic control.

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References

1. C F Claus *Chem. Ber*. **15** 744 (1882)
2. US P. 349981 (1886)
3. US P. 85370 (1868)
4. US P. 118209 (1871)
5. US P. 165802 (1875)
6. M Tessie du Motay, M Marechal *Bull. Soc. Chim. Fr*. **9** 334 (1868)
7. S Z Roginskii, M I Yanovskii, G A Gaziev *Kinet. Katal*. **3** 529 (1962) [a]
8. S Z Roginskii, M I Yanovskii, G A Gaziev *Dokl. Akad. Nauk SSSR* **146** 152 (1962) [b]
9. S Z Roginskii, E I Semenenko, M I Yanovskii *Dokl. Akad. Nauk SSSR* **153** 383 (1963) [b]
10. J M Douglas, D W T Rippin *Chem. Eng. Sci*. **21** 305 (1966)
11. J M Douglas *Ind. Eng. Chem. Proc. Des. Dev*. **6** (5) 42 (1967)
12. C Wandrey, A Renken *Chem.-Ing.-Tech*. **45** 854 (1973)
13. C Wandrey, A Renken *Proceedings GVC/AIChE Joint Meeting* Vol. 1 (Weinheim: Verlag Chemie GmbH, 1974) p. A 3 – 3
14. C Wandrey, A Renken *Chem. Eng. Sci*. **32** 448 (1977)
15. H Helmrich, A Renken, K Schiirgerl *Chem.-Ing.-Tech*. **46** (15) 647 (1974)
16. M P Unni, R R Hudgins, P L Silveston *Can. J. Chem. Eng*. **31** 623 (1973)
17. J E Bailey, F J M Horn *J. Optim. Theory Appl*. **2** 441 (1968)
18. J E Bailey, F J M Horn *AIChE J*. **17** 550 (1971)
19. J E Bailey, F J M Horn *Chem. Eng. Sci*. **21** 109 (1972)
20. J E Bailey, F J M Horn, R C Lin *AIChE J*. **17** 818 (1971)
21. Yu Sh Matros *Nestatsionarnye Protsessy v Khimicheskikh Reaktorakh* (Unsteady Processes in Chemical Reactors) (Novosibirsk: Nauka, 1982)
22. Yu Sh Matros *Kataliticheskie Protsessy v Nestatsionarnykh Usloviyakh* (Catalytic Processes under Unsteady-State Conditions) (Novosibirsk: Nauka, 1987)
23. G K Boreskov, Yu Sh Matros, O V Kiselev, G A Bunimovich *Dokl. Akad. Nauk SSSR* **237** 160 (1977) [b]
24. Yu Sh Matros *Unsteady Processes in Catalytic Reactors* (Amsterdam: Elsevier, 1985)
25. Yu Sh Matros *Catalytic Processes under Unsteady-State Conditions* (Amsterdam: Elsevier, 1989)
26. I A Zolotarskii, Yu Sh Matros *React. Kinet. Catal. Lett*. **3** – **4** 321 (1982)
27. A I Oruzheinikov, Yu V Ivanov, Yu Sh Matros, A P Gerasev *Kinet. Katal*. **27** 954 (1986) [a]
28. I A Zolotarskii, S M Bogdashev, Yu Sh Matros *Kinet. Katal*. **30** 1310 (1989) [a]
29. G K Boreskov *Geterogennyi Kataliz* (Heterogeneous Catalysis) (Novosibirsk: Nauka, 1986)
30. Yu Sh Matros, G A Bunimovich *Catal. Rev. Sci. Eng*. **38** (1) 1 (1996)
31. Yu Sh Matros, A S Noskov, V A Chumachenko *Kataliticheskoe Obezvrezhivanie Otkhodyashchikh Promyshlennykh Gazov* (Catalytic Deactivation of Exhaust Industrial Gas) (Novosibirsk: Nauka, 1991)
32. P L Silveston *Composition Modulation of Catalytic Reactors* (New York: Gordon and Breach, 1998)
33. M M Slin'ko, N I Jaeger *Oscillating Heterogeneous Catalytic Systems* (Amsterdam: Elsevier, 1994)
34. M B Cutlip *AIChE J*. **25** 502 (1979)
35. Y Barshad, E Gulari *AIChE J*. **31** 649 (1985)
36. Y Barshad, E Gulari *J. Catal*. **94** 468 (1985)
37. X Zhou, E Gulari *Chem. Eng. Sci*. **41** 883 (1986)
38. X Zhou, E Gulari *Langmuir* **2** 709 (1986)
39. X Zhou, Y Barshad, E Gulari *Chem. Eng. Sci*. **41** 1277 (1986)
40. G Vaporciyan, A Annapragada, E Gulari *Chem. Eng. Sci*. **43** 2957 (1988)
41. B K Cho *Ind. Eng. Chem. Fundam*. **22** 410 (1983)
42. W R C Graham, D T Lynch *Catalysis on the Energy Scene, Studies in Surface Science and Catalysis* Vol. 19 (Amsterdam: Elsevier, 1984) p. 197
43. F Qin, E E Wolf *Chem. Eng. Sci*. **50** 117 (1995)
44. S C Capsaskis, C N Kenney *J. Phys. Chem*. **90** 4631 (1986)
45. H K Abdul-Kareem, A K Jain, P L Silveston, R R Hudgins *Chem. Eng. Sci*. **35** 273 (1980)
46. S A Ven'yaminov *Mekhanizmy Geterogenno-kataliticheskikh Reaktsii Okisleniya* (Mechanisms of Heterogeneous and Catalytic Oxidation) (Novosibirsk: Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 1993) p. 73
47. V N Tomilov, A N Zagoruiko, S A Ven'yaminov *Tezisy Mezhdunarodnoi Konferentsii 'Khimreaktor-13', Novosibirsk, 1996* (Abstracts of Reports of the International Conference 'Khimreaktor-13', Novosibirsk, 1996) Vol. 2, p. 175
48. M R Prairie, J E Bailey *Chem. Eng. Sci*. **42** 2085 (1987)
49. A Baiker, M Bergougnan *Can. J. Chem. Eng*. **63** 138 (1985)
50. A Baiker, M Bergougnan *Can. J. Chem. Eng*. **63** 146 (1985)
51. A S Rao, K B S Prasad, M B Rao *J. Catal*. **136** 242 (1992)
52. V Stuchly, K Klusacek *Unsteady State Processes in Catalysis* (Utrecht: VSP, 1990) p. 422
53. N L Jaeger, P J Plath, P Svensson *Spatial Inhomogeneities and Transient Behavior in Chemical Kinetics* (Manchester: Manchester University Press, 1990) p. 593
54. M Marwood, F Van Vyve, R Doepper, A Renken *Catal. Today* **20** 437 (1994)
55. A Nappi, L Fabbricino, R R Hudgins, P L Silveston *Can. J. Chem. Eng*. **63** 963 (1985)

56. K G Chanchlani, R R Hudgins, P L Silveston *Can. J. Chem. Eng.* **72** 657 (1994)
57. M A McNeil, R G Rinker *Chem. Eng. Commun.* **127** 137 (1994)
58. H D Wilson, R G Rinker *Chem. Eng. Sci.* **37** 43 (1982)
59. L Chiao, F K Zack, J Thullie, R G Rinker *Chem. Eng. Commun.* **49** 273 (1987)
60. A K Jain, R R Hudgins, P L Silveston *Proceedings of the 7th ISCRE (ACS Symp. Ser.)* Vol. 196 (Washington, DC: American Chemical Society, 1982) p. 97
61. A K Jain, R R Hudgins, P L Silveston *Can. J. Chem. Eng.* **61** 824 (1983)
62. G Rambeau, H Amariglio *Appl. Catal.* **1** 291 (1981)
63. G Rambeau, A Jorti, H Amariglio *Appl. Catal.* **3** 273 (1982)
64. V O Strots, Yu Sh Matros, G A Bunimovich *Chem. Eng. Sci.* **47** 2701 (1992)
65. H A El Masry *Appl. Catal.* **16** 301 (1985)
66. E L Leupold, A Renken *Ger. Chem. Eng.* **1** 218 (1978)
67. BRD P. 2545845; *Chem. Abstr.* **87** 38924 (1977)
68. M A Truffer, A Renken *AIChE J.* **32** 1612 (1986)
69. J Koubek, J Pasek, V Ruzicka *Proceedings of the 7th International Congress on Catalysis, Tokyo, 1980* p. 852
70. J Koubek, J Pasek, V Ruzicka *Catalyst Deactivation* (Amsterdam: Elsevier, 1980) p. 251
71. S Su, P Zasa, A Renken *Chem. Eng. Technol.* **17** 34 (1994)
72. P Zasa, H Randall, R Doepper, A Renken *Catal. Today* **20** 233 (1994)
73. A Renken *Chem. Eng. Sci.* **27** 1925 (1972)
74. H Muraki, Y Fujitani *Ind. Eng. Chem. Prod. Res. Dev.* **25** 414 (1986)
75. B K Cho, B H Shanks, J E Bailey *J. Catal.* **115** 486 (1989)
76. R R Sadhankar, D T Lynch *J. Catal.* **149** 278 (1994)
77. J-P Dath, T Fink, R Imbihl, G Ertl *J. Chem. Phys.* **92** 1582 (1992)
78. T Fink, J-P Dath, M R Bassett, R Imbihl, G Ertl *Surf. Sci.* **245** 96 (1991)
79. S B Schwartz, L D Schmidt *Surf. Sci.* **183** L269 (1987)
80. S B Schwartz, L D Schmidt *Surf. Sci.* **206** 169 (1988)
81. A S A1-Taie, L S Kerschenbaum *Chemical Reaction Engineering-Houston (ACS Symp. Ser.)* Vol. 65 (Washington, DC: American Chemical Society, 1978) p. 512
82. M R Bilimoria, J E Bailey *Chemical Reaction Engineering-Houston (ACS Symp. Ser.)* Vol. 65 (Washington, DC: American Chemical Society, 1978) p. 526
83. C K Lee, J E Bailey *Ind. Eng. Chem. Prod. Res. Dev.* **19** 160 (1980)
84. A Renken *Chem.-Ing.-Tech.* **46** (3) 113 (1974)
85. F Solymosi, A Erdohelyi, A Szke *Catal. Lett.* **32** 43 (1995)
86. F Solymosi, J Cserenyi *Catal. Lett.* **34** 343 (1995)
87. H Amariglio, P Pareja, A Amariglio *Catal. Today* **25** 113 (1995)
88. L Lefort, A Amariglio, H Amariglio *Catal. Lett.* **29** 125 (1994)
89. G E Keller, M M Bhasin *J. Catal.* **73** 9 (1982)
90. C A Jones, J J Leonard, J A Sofranko *Energy Fuels* **1** 72 (1987)
91. Y Mortazavi, R R Hudgins, P L Silveston *Proceedings of the 12th Canadian Symposium on Catalysis, Banff, Alberta, 1992* p. 104
92. Y Mortazavi, R R Hudgins, P L Silveston *Can. J. Chem. Eng.* **74** 683 (1996)
93. A Renken, M Mueller, C Wandrey *Proceedings of the 4th International Symposium on Chemical Reaction Engineering, Dechema, Frankfurt, Germany, 1976* Vol. 3, p. 107
94. D W Park, S Ghazali, G Gau *Appl. Catal.* **6** 175 (1983)
95. B S Balzhinimaev, D W Park, G Gau *React. Kinet. Catal. Lett.* **24** 59 (1984)
96. T Kodama, T Shimizu, T Satoh, K I Shimizu *Energy* **11** 1055 (2003)
97. Y Zeng, S Tamhankar, N Ramprasad, F Fitch, D Acharya, R Wolf *Chem. Eng. Sci.* **58** 577 (2003)
98. V A Sadykov, T G Kuznetsova, S A Veniaminov, D I Kochubey, B N Novgorodov, E B Burgina, E M Moroz, E A Paukshtis, V P Ivanov, S N Trukhan, S A Beloshapkin, Y V Potapova, V V Lunin, E Kemnitz, A Aboukais *React. Kinet. Catal. Lett.* **76** 83 (2002)
99. M Niwa, Y Murakami *J. Catal.* **26** 359 (1972)
100. P L Silveston *Influence of Composition Modulation on Product Yields and Selectivity in the Partial Oxidation of Propylene (Preprint of the 73rd Annual Meeting of American Institute of Chemical Engineers), Chicago, 1980* p. 54
101. P L Silveston, M Forrissier *Ind. Eng. Chem. Prod. Res. Dev.* **24** 320 (1985)
102. Y A Salah-Alhahamed, R R Hudgins, P L Silveston *Chem. Eng. Sci.* **47** 2885 (1992)
103. F Genser, S Pietrzyk *Chem. Eng. Sci.* **54** 4315 (1999)
104. R Grabowski, S Pietrzyk, J Sloczynski, F Genser, K Wcislo, B Grzybowska-Swierkosz *Appl. Catal. A* **232** 277 (2002)
105. V A Doroshenko, L P Shapovalova, L P Dolya *Zh. Prikl. Khim.* **59** 1176 (1986) [c]
106. V P Luk'yanenko, L P Shapovalova, M Yu Kutnaya, V S Solodkaya *Zh. Prikl. Khim.* **60** 1169 (1987) [c]
107. O Rubio, J Herguido, M Menendez *Chem. Eng. Sci.* **58** 4619 (2003)
108. D Creaser, B Andersson, R R Hudgins, P L Silveston *Appl. Catal. A* **187** 147 (1999)
109. V V Sinelnikov, A Yu Stakheev, N N Tolkachev *Proceedings of International Conference 'Chemreactor-17', Athens, 2006* p. 562
110. R K Herz, J B Kleta, J A Sell *Ind. Eng. Chem. Prod. Res. Dev.* **22** 387 (1983)
111. R K Herz *Catalysis Under Transient Conditions (ACS Symp. Ser.)* Vol. 178 (Washington, DC: American Chemical Society, 1982) p. 59
112. R K Herz *Catalysis and Automotive Pollution Control* (Amsterdam: Elsevier, 1987) p. 427
113. L L Hegedus, C C Chang, D J McEwen, E M Sloan *Ind. Eng. Chem. Fundam.* **19** 367 (1980)
114. F Lode, M Houmard, C Migliorini, M Mazotti, M Morbidelli *Chem. Eng. Sci.* **56** 269 (2001)
115. V G Gomes, K W K Yee *Chem. Eng. Sci.* **57** 3839 (2002)
116. G Strohlein, Y Assuncao, R Proplesch, M Mazotti, M Morbidelli *Chem.-Ing.-Tech.* **77** 1819 (2005)
117. S Grüner, A Kienle *Chem. Eng. Sci.* **59** 901 (2004)
118. Can. P. 631882; *Chem. Abstr.* **55** 25158 (1961)
119. US P. 2944627; *Chem. Abstr.* **54** 23491 (1960)
120. E Alpay, C N Kenney, D M Scott *Chem. Eng. Sci.* **48** 3173 (1993)
121. D Chatsiriwech, E Alpay, L S Kershenbaum, C P Hull, N F Kirkby *Catal. Today* **20** 351 (1994)
122. G-h Xiua, P Lia, A E Rodrigues *Chem. Eng. Sci.* **18** 3893 (2002)
123. P L Silveston, R R Hudgins *Chem. Eng. Sci.* **59** 4055 (2004)
124. V P Zakharov, I A Zolotarskii, V A Kuzmin *Chem. Eng. J.* **91** 249 (2003)
125. A S Noskov, L N Bobrova *Proceedings of International Conference on Unsteady-State Processes in Catalysis* (Utrecht: VSP, 1990) p. 665
126. A S Noskov, L N Bobrova, Yu Sh Matros *Catal. Today* **17** 293 (1993)
127. J D Snyder, B Subramaniam *Chem. Eng. Sci.* **53** 727 (1998)
128. D W Agar, W Ruppel *Chem. Eng. Sci.* **43** 2073 (1988)
129. E S Borisova, A S Noskov, L N Bobrova *Catal. Today* **38** 97 (1997)
130. W R Smith, L N Bobrova *Chem. Eng. Sci.* **57** 393 (2002)
131. A S Noskov, L N Bobrova, G A Bunimovich, O V Goldman, A N Zagoruiko, Yu Sh Matros *Catal. Today* **27** 315 (1996)
132. Br. P. 1582441; *Chem. Abstr.* **88** 196888 (1978)
133. US P. 4234549; *Chem. Abstr.* **94** 38453 (1981)
134. Br. P. 2051761; *Chem. Abstr.* **94** 213666 (1981)
135. V M Orlyk, A D Tereshenko, M G Martcenyuk-Kucharuk, A S Vorobey, I A Farafonova *Proceedings of the 1st World Congress on Environmental Catalysis, Roma, 1995* p. 671
136. O S Rabinovich, I G Gurevich, V M Kisarov, G N Toropkina, L I Kalinkina *Materialy Mezhdunarodnoi Konferentsii po Teplomassobmenu, Minsk, 1988* (Proceedings of the International Conference on Heat-mass Exchange, Minsk, 1988) p. 80

137. V M Brovtseva, S M Igolkina, L I Kalinkina, E M Kvashnina, L V Labzova, G N Toropkina *Tezisy Dokladov 5-oi Vsesoyuznoi Konferentsii 'Kataliticheskaya Ochistka Gazov', Tbilisi, 1989* (Abstracts of Reports of the 5th All-Union Conference 'Catalytic Purification of Gases', Tbilisi, 1989) p. 75
138. V E Suprunov *Tezisy Dokladov 4-oi Vsesoyuznoi Konferentsii po Mekhanizmu Kataliticheskikh Reaktsii, Moskva, 1986* (Abstracts of Reports of the 4th All-Union Conference on Mechanism of Catalytic Reactions, Moscow, 1986) Pt. 2, p. 401
139. V E Suprunov *Tezisy Dokladov 3-ei Konferentsii ' Nestatsionarnye Protsessy v Katalize', Novosibirsk, 1986* (Abstracts of Reports of the 3rd Conference 'Unsteady-State Processes in Catalysis', Novosibirsk, 1986) Pt. 1, p. 170
140. L I Kalinkina, V M Kisarov, S M Igolkina, G N Toropkina, E M Kvashnina, I G Gurevich, G A Fateev *Proceedings of International Conference on Unsteady-State Processes in Catalysis, Novosibirsk, Utrecht, 1990* p. 525
141. USSR P. 1674933; *Byull. Izobret*. (33) 40 (1991)
142. A N Zagoruiko, O V Kostenko, A S Noskov *Chem. Eng. Sci.* **51** 2989 (1996)
143. A N Zagoruiko, Doctoral Thesis in Engineering Sciences, Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, 2006
144. A N Zagoruiko, O V Kostenko, P G Tsyrul'nikov, V N Tomilov, V S Sal'nikov, A S Noskov *Khim. Prom-st* **4** 278 (1997) [d]
145. A Salden, G Eigenberger *Chem. Eng. Sci.* **56** 1605 (2001)
146. N V Vernikovskaya, A N Zagoruiko, N A Chumakova, A S Noskov *Chem. Eng. Sci.* **54** 4639 (1999)
147. Russ. P. 2102119; *Byull. Izobret*. (2) 187 (1998)
148. Russ. P. 2147457; *Byull. Izobret*. (11) 131 (2000)
149. A N Zagoruiko *Tezisy Mezhdunarodnoi Konferentsii 'Khimreaktor-14'', Tomsk, 1998* (Abstracts of Reports of the International Conference 'Khimreaktor-14'', Tomsk, 1998) p. 61
150. Russ. P. 2176618; *Byull. Izobret*. (34) 247 (2001)
151. US P. 5487869; *Chem. Abstr*. **124** 298450 (1996)
152. Russ. P. 2263539; *Byull. Izobret*. (31) 449 (2005)
153. *Hydrocarbon Process*. **63** 74 (1984)
154. *Hydrocarbon Process*. **58** 140 (1979)
155. J Wieckowska *Catal. Today* **24** 405 (1995)
156. Russ. P. 2041162; *Byull. Izobret*. (22) 154 (1995)
157. USSR P. 911852; *Byull. Izobret*. (46) 211 (1984)
158. A N Zagoruiko, Candidate Thesis in Chemical Sciences, Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, 1991
159. USSR P. 1701625; *Byull. Izobret*. (48) 78 (1991)
160. USSR P. 1701626; *Byull. Izobret*. (48) 78 (1991)
161. Yu Sh Matros, A N Zagoruiko *Dokl. Akad. Nauk SSSR* **294** 1424 (1987) [b]
162. O V Kiselev, Yu Sh Matros, G A Bunimovich, A S Noskov, A N Zagoruiko, A G Ivanov *Rasprostranenie Teplovykh Voln v Geterogennykh Sredakh* (Heat-Wave Transmission in Heterogeneous Media) (Novosibirsk: Nauka, 1988) p. 203
163. A N Zagoruiko, A S Noskov, V I Drobyshevich, L V Yausheva, I V Malakhova, Yu Sh Matros *Teor. Osnovy Khim. Tekhnol.* **23** 209 (1989) [e]
164. A N Zagoruiko, Yu Sh Matros *Chem. Eng. J.* **87** 73 (2002)
165. G I Brolinskii, O I Sypyak *Razrabotka Tekhnologii Polucheniya Sery Metodom Klausa v Nestatsionarnom Rezhime (Otchet po NIR)* [Development of Technology of Synthesis of Sulfur by the Claus Method in Unsteady Regime (Report on Research Work)]; the article deposited in VINITI, No. 0288.0005770, L'vov, 1987
166. M P Elsner, C Dittrich, D W Agar *Chem. Eng. Sci.* **57** 1607 (2002)
167. M Grunewald, D W Agar *Chem. Eng. Sci.* **59** 5519 (2004)
168. D W Agar *Chem. Eng. Sci.* **54** 1299 (1999)
169. M P Elsner, M Menge, C Mmller, D W Agar *Catal. Today* **79**–**80** 487 (2003)
170. US P. 2979384; *Chem. Abstr*. **55** 21510 (1961)
171. US P. 4439412; *Chem. Abstr*. **98** 128594 (1983)
172. Russ. P. 2088516; *Byull. Izobret*. (24) 298 (1997)
173. Russ. P. 2216506; *Byull. Izobret*. (32) 462 (2003)
174. WO PCT 2004103895; *Chem. Abstr*. **141** 426067 (2004)
175. Russ. P. 2261838; *Byull. Izobret*. (28) 853 (2005)
176. A N Startsev, I I Zakharov, O V Voroshina, A V Pashigreva, V N Parmon *Dokl. Akad. Nauk* **399** 217 (2004) [b]
177. J K Lee, R R Hudgins, P L Silveston *Chem. Eng. Sci.* **16** 2523 (1995)
178. A N Stegasov, V A Kirillov, P L Silveston *Chem. Eng. Sci.* **49** 3699 (1994)
179. Y X Li, Z M Cheng, L H Liu, W K Yuan *Chem. Eng. Sci.* **10** 1571 (1999)
180. J P Briggs, R R Hudgins, P L Silveston *Chem. Eng. Sci.* **32** 1087 (1977)
181. Russ. P. 2085481; *Byull. Izobret*. (21) 263 (1997)
182. N V Vernikovskaya, A N Zagoruiko, A S Noskov *Chem. Eng. Sci.* **54** 4475 (1999)
183. G A Bunimovich, N V Vernikovskaya, V O Strots, B S Balzhinimaev, Yu Sh Matros *Chem. Eng. Sci.* **50** 565 (1995)
184. B S Balzhinimaev, A A Ivanov, O B Lapina, V M Mastikhin, K I Zamaraev *Faraday Discuss. Chem. Soc.* **87** 133 (1989)
185. A R Brun-Tsekhovoi, Doctoral Thesis in Chemical Sciences, Institute of Petrochemical Synthesis, Moscow, 1990
186. S S Kurdyumov, A R Brun-Tsekhovoi, A L Rosental *Pet. Chem.* **36** 139 (1996)
187. B Balasubramanian, A Lopez Ortiz, S Kaytakoglu, D P Harrison *Chem. Eng. Sci.* **15**–**16** 3543 (1999)
188. Y Ding, E Alpay *Chem. Eng. Sci.* **18** 3929 (2000)
189. G-h Xiua, P Lia, A E Rodrigues *Chem. Eng. J.* **1**–**3** 83 (2003)
190. E Ochoa-Fernandez, H K Rusten, H A Jakobsen, M Ronning, A Holmen, D Chen *Catal. Today* **106** 41 (2005)
191. D K Lee, I H Baek, W L Yoon *Chem. Eng. Sci.* **59** 931 (2004)
192. K Johnsen, H J Ru, J R Grace, C J Lim *Chem. Eng. Sci.* **61** 1195 (2006)
193. A G Okunev, V E Sharonov, Yu I Aristov *Tezisy Dokladov II Vserossiiskogo Seminara 'Toplivnye Elementy i Energoustanovki na ikh Osnove', Novosibirsk, 2003* (Abstracts of Reports of IInd All- Union Seminar 'Fuel Cells and Energy Installations Based on Them'), Novosibirsk, 2003) p. 124
194. Ch Han, D P Harrison *Chem. Eng. Sci.* **24** 5875 (1994)
195. B T Carvill, J R Hufton, M Anand, S Sircar *AIChE J.* **42** 2756 (1996)
196. J Xu, G F Froment *AIChE J.* **35** 89 (1989)
197. V Hacker *J. Power Sources* **118** 311 (2003)
198. V Galvita, K Sundmacher *Proceedings of International Conference 'Chemreactor-17', Athens, 2006* p. 132
199. M Ryden, A Lyngfelt *Int. J. Hydrogen Energy* **31** 1271 (2006)
200. F J Derbyshire, D L Trimm *Carbon* **13** 189 (1975)
201. R T K Baker, M A Barber, P S Harris, F S Feates, R J Waite *J. Catal.* **26** 51 (1972)
202. A Sacco, P Thacker, T N Chang, A T S Chiang *J. Catal.* **85** 224 (1984)
203. P K de Bokx, A J H M Kock, E Boellaard, W Klop, J W Geus *J. Catal.* **96** 454 (1985)
204. L B Avdeeva, O V Goncharova, D I Kochubey, V I Zaikovskii, L M Plyasova, B N Novgorodov, Sh K Shaikhutdinov *Appl. Catal. A* **141** 117 (1996)
205. Z R Ismagilov, N V Shikina, V N Kruchinin, N A Rudina, V A Ushakov, N T Vasenin, H J Veringa *Catal. Today* **102**–**103** 85 (2005)
206. N Muradov, F Smith, A T Raissi *Catal. Today* **102**–**103** 225 (2005)
207. M A Ermakova, D Yu Ermakov, G G Kuvshinov *Appl. Catal. A* **201** 61 (2000)
208. T V Reshetenko, L B Avdeeva, Z R Ismagilov, A L Chuvilin, V B Fenelonov *Catal. Today* **102**–**103** 115 (2005)
209. T V Reshetenko, L B Avdeeva, Z R Ismagilov, V V Pushkarev, S V Cherepanov, A L Chuvilin, V A Likholobov *Carbon* **41** 1605 (2003)
210. H J Richter, K F Knocke *Inositol Phosphates and Derivatives (ACS Symp. Ser)* (Washington, DC: American Chemical Society, 1983) Vol. 235, p. 71
211. M Ishida, D Zheng, T Akehata *Energy* **12** 147 (1983)
212. M Ishida, J Hin *Ind. Eng. Chem. Res.* **35** 2469 (1996)

213. R Villa, C Cristiani, G Groppi, L Lietti, P Forzatti, U Coronaro, S Rossini *J. Mol. Catal. A* **204** – **205** 637 (2003)
214. A N Zagoruiko *Proceedings of International Conference 'Chemreactor-16', Berlin, 2003* p. 202
215. A N Zagoruiko *Teor. Osnovy Khim. Tekhnol.* **39** 72 (2005) [e]
216. A N Zagoruiko *Chem. Eng. J.* **107** 133 (2005)
217. A N Zagoruiko *Proceedings of International Conference 'Chemreactor-17', Athens, 2006* p. 169
218. US P. 5530171; *Chem. Abstr.* **125** 11415 (1996)
219. R K Grasselli, D L Stern, G G Tsykoyannis *Appl. Catal. A* **189** 9 (1999)
220. R M Contractor *Chem. Eng. Sci.* **22** 5627 (1999)
221. A A Ivanov *Mekhanizmy Geterogenno-kataliticheskikh Reaktsii Okisleniya* (Mechanisms of Heterogeneous and Catalytic Reactions of Oxidation) (Novosibirsk: Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 1993) p. 103
222. US P. 6291686; *Chem. Abstr.* **132** 153651 (2001)
223. R M Heck, R J Farrauto *Appl. Catal. A* **221** 443 (2001)
224. M Shelef, R W McCabe *Catal. Today* **26** 35 (2000)
225. T V Pavlova, N V Vernikovskaya, N A Chumakova, A S Noskov *Trudy Pervoi Shkoly-konferentsii 'Dizain Katalizatorov', Novosibirsk, 2006* (Proceedings of the First School-Conference 'Design of Catalysts', Novosibirsk, 2006) p. 244
226. W S Epling, L E Campbell, A Yezerets, N W Currier, J E Parks *Catal. Rev. Sci. Eng.* **46** 163 (2004)
227. US P. 6314722; *Chem. Abstr.* **135** 361806 (2001)
228. D Agar *Proceedings of International Conference 'Recovery, Recycling, Reintegration', Geneva, 1997* Vol. 4, p. 45
229. U Nieken, O Watzenberger *Chem. Eng. Sci.* **54** 2619 (1999)
230. A Breed, M F Doherty, S Gadewar, P Grosso, I M Lorkovic, E W McFarland, M J Weiss *Catal. Today* **106** 301 (2005)
231. M Kuczynski, M H Oyevaar, R T Pieters, K R Westerterp *Chem. Eng. Sci.* **42** 1887 (1987)
232. S Goto, T Tagawa, T Oomiya *Chem. Eng. Essay* **19** 978 (1993)
233. E A Ivanov, S I Reshetnikov, M V Sidyakin, A N Startsev *React. Kinet. Catal. Lett.* **2** 389 (2003)
234. K S Gulyaev, Candidate Thesis in Chemical Sciences, Omsk Branch of Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Omsk, 1997

[a] — *Kinet. Catal. (Engl. Transl.)*
[b] — *Dokl. Phys. Chem. (Engl. Transl.)*
[c] — *Russ. J. Appl. Chem. (Engl. Transl.)*
[d] — *Ind. Chem. (Engl. Transl.)*
[e] — *Theor. Found. Chem. Eng. (Engl. Transl.)*