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Catalysts and Processes for Paraffin and Olefin Dehydrogenation[1]

R. A. Buyanov and N. A. Pakhomov
Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

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Abstract—General trends in the development of industrial processes and catalysts for the dehydrogenation of lower C_3–C_5 paraffins and olefins are considered. A brief review of studies on the improvement of commercial nickel–calcium phosphate and iron oxide catalysts for the dehydrogenation of olefins and ethylbenzene to dienes and styrene, respectively, performed in the Laboratory of Dehydrogenation at the Boreskov Institute of Catalysis (Siberian Division, Russian Academy of Sciences) in collaboration with OAO NPO Yarsintez is given. The results of studies on the development of new spinel-supported bimetallic Pt–Sn catalysts for the steam dehydrogenation of lower paraffins are presented.

INTRODUCTION

Olefins and dienes (propylene, *n*-butenes, isobutylene, butadiene, isoprene, styrene, and its derivatives) are in considerable current use in various chemical industries for the production of synthetic rubbers, plastics, automotive fuel components (methyl *tert*-butyl ether (MTBE), *tert*-amyl methyl ether, and alkylates), and other valuable chemical products. For this reason, there has been considerable interest worldwide in intensifying their production within the last half a century. Catalytic dehydrogenation is one of the most important among currently available methods. Therefore, the number of studies on the improvement of old and the development of new dehydrogenation catalysts remains high. The results of these studies were summarized in several reviews and monographs [1–3]. However, some of the reviews appeared more than 20 years ago, and it seems reasonable to consider current trends in this area and analyze the results concerning the improvement and development of new domestic dehydrogenation catalysts and processes.

1. TRENDS IN THE DEVELOPMENT OF DEHYDROGENATION METHODS AND CATALYSTS

The processes of catalytic dehydrogenation of lower paraffins, olefins, and alkylaromatic hydrocarbons have the highest throughputs in the world chemical industry. The development of dehydrogenation methods in Russia was different from that in Western countries at the same time. With the exception of the 1990s, the years of reforms,[2] monomers for synthetic rubber were synthesized in Russia by dehydrogenation methods. There are at least two reasons for that. One is the availability of the unique reserves of C_3–C_5 hydrocarbons in petroleum and gas condensate produced in Russia. The other is due to the fact that synthetic rubber production was ahead of the development of pyrolysis methods, although the fraction of monomers obtained from pyrolysis products has been constantly increasing. Many research teams at various research institutions were involved in the design of domestic processes and catalysts for dehydrogenation. Among the best-known institutes are OAO NPO Yarsintez (the former Research Institute of Monomers for Synthetic Rubber), the Boreskov Institute of Catalysis, the Zelinskii Institute of Organic Chemistry, the All-Union Research Institute of Olefins, and the All-Union Research Institute of Synthetic Rubber. The Research Institute of Monomers for Synthetic Rubber was the leading applied-research institute in this field. All commercial dehydrogenation catalysts used in recent years were developed at this institute in collaboration with other organizations, including the Boreskov Institute of Catalysis.

The situation was somewhat different in Western countries. Intensive studies of dehydrogenation and the applications of new catalysts peaked in the late 1950s and the early 1960s. Steam crackers (SCs) and fluidized catalytic crackers (FCCs) became the main sources of lower olefins and dienes later. The production of olefins using catalytic dehydrogenation gradually declined. Some companies retained only several plants butadiene synthesis.

In the mid-1980s, a trend became evident in the world petrochemical industry toward an increase in the propylene and isobutylene demand, which could not be fulfilled by an increase in the capacities of SC and FCC processes. An increase in the consumption of propylene was primarily associated with its increased use for polypropylene production. This trend also remained in the 1990s. By the early 1990s, the “chemical” propy-

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[1] Proceedings of Nizhnekamsk Seminar on Catalysis (March 15–17, 2000).

[2] A dramatic situation in the production of monomers for synthetic rubber in Russia during these years was strikingly described by Liakumovich *et al.* [4] using OAO Nizhnekamskneftekhim as an example.

lene production profile was 70% SC, 23% FCC, and 7% propane dehydrogenation [5]. The amount of SC-produced propylene depends on the feedstock and is related to the amount of produced ethylene, which is the main product of SC. Because both the feedstock and the amount of ethylene were determined by the demand for polyethylene, the amount of pyrolytic propylene was fixed. Consequently, the demand for propylene could not be satisfied. FCC propylene is primarily consumed for the manufacture of polymer gasoline, motor alkylates, and cumene. For this reason, propane dehydrogenation is the most important additional source of propylene [5].

The demand for isobutylene increased drastically when MTBE started to be used as a gasoline component. MTBE is produced by the etherification of isobutylene and methanol. A dramatic increase in the use of MTBE in the United States was stimulated by the Clean Air Act Amendments, which prescribed the use of oxygen-containing substances in reformulated gasoline[3]. In other regions, for example, in Europe and Russia, MTBE is use to replace of tetraethyl lead and benzene to increase the octane number of gasoline.

The demand for isobutylene for MTBE synthesis grew even more rapidly than the demand for propylene. Table 1 summarizes data on the worldwide increase in the demand for isobutylene and MTBE in the last decade and on the sources of isobutylene [7]. These data indicate that the use of MTBE will almost triple by the end of this century. At first glance, it seems that the demand for isobutylene for MTBE could be met by SC and FCC processes. However, isobutylene production by the plants with SC and FCC units is oriented toward butyl rubber, polyisobutylene, and other manufactures. Thus, an increase in the use of isobutylene should also be maintained by an increase in its production by catalytic dehydrogenation units.

The above factors formed the basis for a rapid growth of new catalysts and processes for the dehydrogenation of lower C_3–C_5 paraffins in Western countries in recent years.

In the last few years, the same trends toward an increased use of isobutylene and propylene are seen in Russia against the background of synthetic rubber production decline, the reasons for which are subjective rather than objective. Undoubtedly, this will reanimate research and development in the field of new dehydrogenation catalysts.

2. MODERN INDUSTRIAL DEHYDROGENATION CATALYSTS AND PROCESSES

Specific features of dehydrogenation reactions determine the reaction conditions, process design, and the nature of catalysts. Thus, paraffin and olefin dehydrogenation reactions are highly exothermic, and the yields of target products are limited by reaction equilibria [1]. Reasonable yields of target products are attained at temperatures higher than 520 and 570°C in paraffin and olefin dehydrogenation, respectively. For this reason, dehydrogenation processes are performed at temperatures as high as 550–620°C; in this case, cracking and carbon deposition on the catalyst surface occur at noticeable rates. The thermodynamic characteristics of olefin and ethylbenzene dehydrogenation are particularly unfavorable. To decrease the partial pressure of initial hydrocarbons and to increase the yield of target products, the feed is diluted with steam, which also serves as a heat-transfer agent. Paraffins are dehydrogenated at near-atmospheric pressures or in a vacuum.

The following main dehydrogenation catalysts have been in commercial use:

(1) Chromia–alumina catalysts for the dehydrogenation of lower C_3–C_5 paraffins;

(2) Supported modified platinum catalysts for the dehydrogenation of lower paraffins;

(3) Phosphate catalysts for the dehydrogenation of C_4–C_5 olefins; and

(4) Iron oxide catalysts for the dehydrogenation of alkylaromatic hydrocarbons and C_4–C_5 olefins.

The above list reveals the following characteristic feature. Although dehydrogenation reactions seem to be similar (a paraffin or olefin eliminates a hydrogen molecule), these reactions occur on chemically different catalysts. The following rule is applicable: catalysts that are highly active in olefin dehydrogenation exhibit low activity at the first stage of paraffin dehydrogenation. The reverse is not so evident. Indeed, neither chromia–alumina catalysts nor platinum catalysts are commercially used as olefin dehydrogenation catalysts. The chromia–alumina catalysts cannot be used because

Table 1. World consumption of isobutylene and MTBE (thousand tons per year) [7]

Year	1990	1995	2000
Consumption of MTBE	8.3	19.8	22.0
Consumption of isobutylene for MTBE	5.3	12.7	13.8
Isobutylene sources:			
catalytic cracking (FCC)	8.3	9.2	9.8
steam cracking (SC)	3.2	3.7	3.8
dehydration of *tert*-butanol	2.2	2.2	2.2
dehydrogenation of isobutane	1.1	8.5	9.7
Total	14.8	23.6	25.5

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[3] Recently, it was reported that MTBE was found in ground and open water in the United States due to its leaking from underground storage tanks for reformulated gasoline [6]. This stirred up environmental activity of MTBE opponents. The use of MTBE was prohibited in California starting from December 31, 2002.

they are completely poisoned by steam. However, these catalysts are highly efficient in the processes of single-step vacuum dehydrogenation of paraffins to dienes [1]. Supported platinum catalysts can also be efficient in single-stage diene synthesis from paraffins; in this case, the partial pressure can be lowered by diluting the feed with steam [8, 9].

Four variants of lower paraffin dehydrogenation are currently used in industry:

1. Catofin process of isobutane or propane dehydrogenation (ABB Lummus Crest/United Catalysts). The process is performed in a vacuum in adiabatic fixed-bed reactors with a chromia–alumina catalyst. This process is a prototype of the 40-year-old Catadiene process for the single-stage vacuum dehydrogenation of *n*-butane to butadiene, which was initially used by Houdry and then by Air Products. Presently, two petrochemical plants operate in Tobolsk and Nizhnekamsk in Russia. An imported chromia–alumina catalyst is used at this plants.[4] In the Catadiene and Catofin processes, the heat released from carbon deposits in the course of catalyst regeneration is used to perform endothermic dehydrogenation reactions. Therefore, the process is performed in short dehydrogenation–regeneration cycles (20–30 min each), and a great number of reactors are required for continuous process operation.

The Catofin process for isobutylene production was commercialized in the middle of 1986 at a plant of Texas Petrochemical Co. By the year 1992, four units for isobutylene production and a unit for propylene production licensed by ABB Lummus Crest/United Catalysts operated worldwide.

2. Fluidized-bed process of dehydrogenation with a microspheric chromia–alumina catalyst. In this process, the catalyst circulates between a reactor and a regenerator, and the heat of carbon burning is used to perform an endothermic dehydrogenation reaction. In the plants of the Russian Federation, the IM-2201-M catalyst is used for *n*-butane and isopentane dehydrogenation; this catalyst is characterized by low abrasion strength. For the fluidized-bed dehydrogenation of isobutane in the analogous FBD process (Snamprogetti–Yarsintez), an improved SPS Al–Cr catalyst is used, which exhibits a higher mechanical strength [10, 11]. This catalyst is currently used in the units of the Omsk Synthetic Rubber Plant. Export versions of this catalyst under the trade names FBD-3 and FBD-4 have been used in Saudi Arabia since 1997. The fluidized-bed technology is well developed. It is characterized by the lowest capital outlays, power intensity, and low product cost among process variants [10]. Nevertheless, this process does not seem to be promising because the catalyst is environmentally dangerous and abradable since it involves carcinogenic hexavalent chromium. Thus, a finely divided chromium-containing fraction should permanently be retained in the cycle. Another important problem is the disposal of spent catalysts and finely divided phases formed in the process.

The above problems served to motivate UOP, which used and licensed a process of this type since the 1940s, to repudiate this process in the 1970s when this company started to advertise the new Oleflex process, which is environmentally safer [5].

3. Oleflex process (UOP). This process for isobutane and propane dehydrogenation was first introduced in Thailand in 1990 [5, 12]. The process was developed on the basis of the following two successfully operating UOP processes: the Pacol process for the dehydrogenation of paraffins from the kerosene fraction to monoolefins and the CCR platforming process for the reforming of naphtha in the production of high-octane gasoline. The Oleflex process is performed with a moving bed of a bead platinum catalyst in a multiple-stage reactor unit via a reactor–regenerator circuit with intermediate heat absorption between the steps. Three or four reactors are required for ~40% conversion in the dehydrogenation of isobutylene or propane, respectively.

This process is characterized by high capital outlays because of sophisticated apparatus. Moreover, this technology requires a high mechanical strength of the catalyst. It is likely that, for the above reasons, the first plant in Thailand was put into operation with a 10-year delay in spite of booming publicity program.

4. Steam active reforming (STAR) process of Phillips Petroleum Co. This process is performed in the fixed bed of a catalyst. The platinum catalyst supported on spinel [13] is placed inside tubes heated by flue gases. The process is characterized by sophisticated apparatus. According to promotional materials of the company, this process was scheduled for commercialization in as early as 1992. However, until recently, there was no information on the industrial implementation of this process. Only the *Oil and Gas Journal* [14] reported on the project of Polibutenos Argentinos S.A., according to which a plant for isobutylene dehydrogenation by the STAR process with the annual capacity 40 000 ton was scheduled to be put in operation in 1994. In this case, the catalyst was expected to operate in 7–8-h cycles with 1-h regeneration.

Table 2 summarizes the main characteristics of the Catofin, Oleflex, STAR, and FBD processes. The information on plants that were in operation or projected in the 1990s can be found in [15, 16].

A new single-stage process for the steam dehydrogenation of isopentane to isoprene at an atmospheric pressure has no analogs in the world industry. This process and the IM-22101 catalyst were developed by the Boreskov Institute of Catalysis in collaboration with OAO NPO Yarsintez. Spinel-supported platinum modified with tin additives is used as a catalyst [8]. The process is performed as short dehydrogenation–regeneration cycles in an adiabatic fixed-bed reactor. The per-pass yield of isoprene is at least 14.5 wt % at 82–84 wt % selectivity

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[4] Unfortunately, all attempts to develop a domestic catalyst for this process failed.

for dehydrogenation products. The consumption of the catalyst is 0.8 kg per ton of product. The consumption of isopentane is 1.65 ton per ton of isoprene.

The main performance characteristics of this process are better than for the current two-stage method for isoprene production, the single-stage method for vacuum dehydrogenation of isopentane, and the formaldehyde method for isoprene production [8].

According to Pakhomov *et al.* [17], the slightly modified IM-22101 catalyst is efficient in isobutane dehydrogenation to isobutylene, the demand for which is growing. The new catalyst is characterized by a low platinum concentration (0.15–0.20 wt %) and thermal stability up to 800°C. The physicochemical properties of this catalyst will be considered in more detail in Section 3.4 below.

In Russia, the commercial dehydrogenation of olefin hydrocarbons is industrially implemented in two-stage processes of butadiene and isoprene production from the corresponding paraffins. The dehydrogenation processes can be carried out according the following two variants [1, 18]: (1) dehydrogenation in short 10–15-min cycles (a dehydrogenation cycle and a regeneration cycle with the intermediate purging with an inert gas or steam), and (2) continuous dehydrogenation in a self-regeneration mode. Fixed-bed reactors are used in both cases. The choice of the variant depends on the catalyst. Thus, the IM-2204 phosphate catalysts are highly active, but they are rapidly coked. Therefore, they are used in the first variant. To perform the overall process in a continuous mode, the unit consists of two reactors: one of them is used for dehydrogenation and the other operates during regeneration with air. A changeover from the dehydrogenation mode to purging and regeneration is automated using high-temperature hydraulic valves. Under industrial conditions, the process is performed at 570–630°C with the dilution of feed with steam in a ratio of 1 : 20.

The second variant of the process for isoamylene dehydrogenation was commercialized very recently and uses the K-24 iron oxide catalyst, which is also applicable to ethylbenzene dehydrogenation to styrene [18]. Iron oxide catalysts can operate in a self-regeneration mode for a long time with the dilution of the feedstock with steam. For this reason, catalyst regeneration with air was eliminated from the process, and only steam regeneration was performed when necessary or when performance characteristics stably become worse. In this case, only one reactor is in service.

Aminova and Bazhenov compared the properties of domestic K-24-I, IM-2204, and IM-2204-M catalysts under industrial conditions [19]. They found that these catalysts were most efficient in isoprene synthesis from isopentane in a two-stage process. Kotelnikov [10] also suggests that the improved K-28 iron oxide catalyst for ethylbenzene dehydrogenation to styrene has better characteristics tan all its analogs.

3. DEVELOPMENT AND IMPROVEMENT OF DOMESTIC DEHYDROGENATION CATALYSTS

We participated in the development of a number of new catalysts and in the improvement of some of the above catalysts in collaboration with researchers from OAO Yarsintez. Because domestic catalysts for paraffin

Table 2. Comparison of current industrial technologies for the dehydrogenation of lower paraffins

Process	Catofin	Oleflex	STAR	FBD
License holder	“United Catalysts/Lummuss Crest”	UOP	“Phillips Petroleum”	“Snamprogetti–Yarsintez”
Operating mode	Cyclic	Moving bed	Cyclic	Fluidized bed
Reactor type	Adiabatic	Adiabatic	Isothermal	Adiabatic
Total number of reactors	5	4	8	1
Duration of a dehydrogenation–regeneration cycle	25 min	Continuous	8 h	Continuous
Process conditions:				
T, °C	525–677	525–705	482–621	520–600
Pressure, atm	0.1–0.7	1–3	3–8	1.1–1.5
Diluent : hydrocarbon, mol/mol	0	1*	2**	0
Propylene production				
propane conversion, %	65	40	30–40	
selectivity for C_3H_6, %	87	90	80–90	
Isobutylene production				
isobutane conversion, %	60–65	45–50	45–55	≈50
selectivity for iso-C_4H_8, %	95	91–92	85–90	>90

* Hydrogen is the diluent.

** Steam is the diluent.

and olefin dehydrogenation are highly competitive with their world analogs, we dwell on the scientific aspects of the development of these catalysts and consider the most interesting findings that formed the basis for the development of these catalysts.

3.1. Scientific and Methodological Aspects of Studies

Commercial catalysts for the dehydrogenation of olefins and alkylaromatic hydrocarbons usually contain several components. Thus, early phosphate catalysts contained phosphorus compounds of nickel, calcium, chromium, and zirconium. The iron–potassium systems contained chromium and silicon additives. By the time the studies at the Boreskov Institute of Catalysis began, all conceivable empirical procedures for the improvement of these catalysts, such as introducing promoters or changing preparation procedures, were practically exhausted.

For this reason, we formulated a methodology, which was subsequently used to improve commercial catalysts [20] and develop new catalytic systems [9].

Our methodology was formulated as follows.

- The primary task was to determine the active component (or phase) of a catalyst in a particular reaction and the roles of all other catalyst components.
- The next task, which is related to the first one, is to examine the phase transformations of the catalyst at all stages of its preparation and operation. In this case, the phase and chemical compositions and the structures of compounds formed at all stages are determined. The preparation conditions (method, temperature, gaseous medium, etc.) favorable for the preparation of the active component with a specified composition and structure are to be found.
- Simultaneously with solving the second task, the genesis of a catalyst texture is studied. For bulk systems, the texture means the specific surface area, volume, and pore size of a catalyst. For supported systems, in addition to the above characteristics, the dispersity of a supported active component and its distribution over support grains are also important.
- Then, the temperature range and service life limits, in which the phase composition and texture remain stable, are determined.
- Note that in some catalytic systems only *in situ* studies using physical techniques should be performed. Thus, in the case of iron oxide catalysts, high-temperature X-ray diffraction in various gas media showed that the phase composition of the catalyst changes when it is removed from a catalytic reactor and studied in air.

Within the framework of the above methodology, we found the best composition and preparation conditions for various catalysts and developed a number of new commercial modifications, which either exhibited better catalytic properties and other service properties or were easier to prepare.

To illustrate the above methodology, we consider the improvement of commercial phosphate and iron oxide catalysts for olefin dehydrogenation and the development of a new supported platinum catalyst for the steam dehydrogenation of lower paraffins.

3.2. Improvement of a Phosphate Catalyst

Extensive studies on phosphate catalysts performed by the late 1960s in various countries made it possible to empirically choose the preparation and working conditions [2]. In these years, the best characteristics were achieved on the foreign Dow-B catalyst and the domestic KNF catalyst. However, it was impossible to explain a number of properties of these catalysts and determine how they can further be improved. Thus, in particular, in addition to an improvement of the catalytic activity and selectivity of KNF, it was necessary to solve the problem of the frequent irreproducibility of the prepared batches, increase the mechanical strength, and prolong the service life of the catalyst. Moreover, it was unknown why considerable dilution (up to 1 : 20) of feed with steam was required, and why the catalyst was deactivated as the degree of dilution was decreased or the dehydrogenation time was increased.

The genesis of the phase composition was examined and the composition of the active components of these catalysts was determined in our laboratory using a set of physical techniques [21–24]. It was found that two phases essentially different in the chemical composition and structure were present in the catalysts. Consequently, the roles of these phases in the catalysts were radically different. The inactive phase of calcium phosphate with the whitlockite structure and the active phase of nickel pyrophosphate $Ni_2P_2O_7$ or a solid solution of chromium on its basis were detected. The crystal lattice of whitlockite is stabilized by nickel and chromium ions. The composition of these compounds is described by the formulas $Ca_{18}Ni_2H_2(PO_4)_{14}$ and $Ca_{18}Cer_{1.33}H_2(PO_4)_{14}$. All other compounds that can be present in the catalyst (free nickel, chromium, and calcium oxides; chromium and calcium phosphates; calcium pyrophosphate; and nickel–chromium spinel) are undesirable impurities, which can impair the catalytic activity and selectivity. In this connection, the conditions for catalyst preparation were found, which eliminated the formation of impurities in noticeable amounts. It was also found that in the course of catalyst preparation the active phase becomes supported on whitlockite crystals. On the basis of these data, it was hypothesized that the active phase is fixed on the surface of whitlockite via nickel ions, which have bonds in the crystal lattices of both nickel pyrophosphate and whitlockite. Thus, the role of whitlockite as a support for the active component in phosphate catalysts was first revealed.

The detection of whitlockite in the catalyst composition made it possible to determine the factors affecting its formation. It was found that the temperature ranges of whitlockite crystallization and the number of stabilizing ions in the lattice strongly depend on the composition of medium where a freshly prepared catalyst was thermally activated. The formation of the whitlockite structure in calcium phosphates in the presence of chromium compounds was finished at 850°C; in this case, hydrogen was retained in the HPO_4^{2-} groups. In the presence of nickel compounds, whitlockite was formed at 600–650°C. On heating in steam, chromium was displaced from the crystal lattice of whitlockite; the concentration of nickel in the whitlockite crystal lattice increased. The crystallization of the active component as a solid solution of chromium in nickel pyrophosphate took place in the catalyst at 800°C. At 850°C, chromium began to release from the pyrophosphate lattice.

It was also found that the tested catalyst is thermodynamically unstable under industrial dehydrogenation conditions and undergoes reduction. As the duration of dehydrogenation was prolonged or the degree of dilution of *n*-butenes with steam was decreased, the reduction was accompanied by the appearance of metallic nickel, which resulted in the dramatic carbonization of the catalyst. Whitlockite stabilized with nickel ions is the initial source of metallic nickel. Then, the active component also becomes involved in the reduction process. Note that the emergence of metallic nickel from the whitlockite structure is irreversible under the above hydrogenation conditions, and the subsequent oxidative regeneration of the catalyst does not recover the initial composition of the catalyst. This irreversibly deteriorates the catalyst characteristics. Thus, the conditions of dehydrogenation (duration and minimum dilution of the feed with steam) were explained.

Experimental data considered above formed the basis for improving the technology for KNF catalyst preparation. All improvements were made without changing the bulk chemical composition of the catalyst. Thus, the use of an electrochemical technique for producing nickel–chromium phosphate simplified the preparation procedure (it became possible to pour only two solutions of nickel–chromium phosphate and calcium nitrate in the course of coprecipitation) and resulted in the complete homogenization of a paste at the stage of preparation. Finally, the use of the electrochemical technique resulted in the predominant stabilization of whitlockite by chromium, which in turn caused a redistribution of nickel between the support and the active component. The activity and selectivity of the phosphate catalyst increased because of this redistribution.

The electrochemical preparation of nickel–chromium phosphate formed the basis for a preparation procedure for the new modification of a phosphate catalyst IM-2204 [25]. Table 3 demonstrates that the performance characteristics of this catalyst are much better than the properties of Dow-B and KNF catalysts.

Knowledge of the temperature ranges of the crystallization of the main phases in the catalyst made it possible to suggest a more rapid and easy procedure for activating the catalyst and improve its mechanical strength. This procedure includes precipitation, drying, calcination at temperatures close to the temperature of formation of whitlockite with chromium (600–620°C), grinding, and pelletization with the addition of graphite. After loading into a reactor, the catalyst is heated with steam at 750°C for 2–4 h. The new formation and activation procedures formed the basis for the preparation of the IM-2206 modification [26]. This activation significantly increased the mechanical strength and prolonged the service life of the catalyst; the space velocities of feed increased from 150 to 300 h^{-1}. The productivity of reactors and operating plants increased by 40–50% and 25%, respectively, without capital outlays for reequipment.

A study of conditions for the formation of the active component, nickel–chromium phosphate, demon-

Table 3. Performance characteristics of phosphate catalysts in the processes of butylene and isoamylene dehydrogenation

Catalyst	Feedstock	Catalytic characteristics*		Service life	Improved parameter
		X, %	*S*, wt %		
Dow-B (USA)				5000 h	
	Butylenes	38	89		–
KNF				4000 h	
	Butylenes	37	85		–
	Isoamylenes	38	86		
IM-2204				5000–7000 h	Use of the electrochemical preparation of nickel–chromium phosphate
	Butylenes	40	85		
	Isoamylenes	43	87		
IM-2206				Longer than two years	Use of a new molding technique for increasing the mechanical strength Addition of a stage of high-temperature steam activation for producing an optimum texture Addition of zirconium for improving the thermal stability
	Butylenes	46	86		
	Isoamylenes	45	88		

* *X* is the degree of conversion, and *S* is the selectivity for butadiene or isoprene, respectively.

Table 4. Catalytic properties of alkali metal ferrites in the reactions of *n*-butene dehydrogenation [27]

Active component	Conversion, %	Selectivity, mol %
$KFeO_2$	30.4	85.1
$KFeO_2$–SiO_2		
$RbFeO_2$	35.5	78.9
$RbFeO_2$–SiO_2	39.6	80.1
$CsFeO_2$	44.2	76.5
$CsFeO_2$–SiO_2	49.0	78.5

strated that the steam crystallization at 800–820°C could additionally increase the catalyst activity by 15–20%. Moreover, the introduction of the stage of high-temperature steam treatment increased the rate of formation of the optimal-texture catalyst. This made it possible to eliminate the stage of catalyst activation in an industrial reactor before reaching the operating conditions. Previously, this stage took two to four weeks.

3.3. Improvement of Catalysts Based on Alkali Metal Ferrites

Catalysts based on alkali metal ferrites are commercially prepared by the wet mixing of components to form a plastic mixture followed by the formation of the paste as extrudates. Iron oxide and potassium carbonate are used as starting components. Silicon compounds as potassium silicates are also introduced into the initial mixture. Studies performed in our laboratory, which were summarized in a review paper [20], demonstrated that the potassium ferrite $KFeO_2$ or its solid solution with silicon oxide is an active component of iron–potassium catalysts in dehydrogenation reactions. Studies in a high-temperature X-ray chamber showed that the active component is formed in the solid-phase reactions

$$K_2CO_3 + \alpha\text{-}Fe_2O_3 \longrightarrow 2KFeO_2 + CO_2,$$

$$K_2SiO_3 + \alpha\text{-}Fe_2O_3$$

$$\longrightarrow 2KFeO_2 - SiO_2 \text{ (solid solution).}$$

The formation of potassium ferrite is significantly favored on calcination in a steam atmosphere: the temperature of the onset of reaction decreases by 150–200 K, and the reaction proceeds to a higher degree.

In studies of the stability of the phase composition of the catalyst in various media, it was found that pure potassium ferrite undergoes reduction under the conditions of *n*-butene dehydrogenation at a molar H_2O/C_4H_8 ratio lower than 15. The addition of silicon compounds to the catalyst stabilizes the phase composition in the reaction medium, and the $KFeO_2$–SiO_2 solid solution is not reduced even at $H_2O/C_4H_8 = 6$. The yield of target products increases when the feedstock is diluted with steam. Moreover, steam is a heat-transfer agent, and the catalyst exhibits self-regenerating properties in its presence. Therefore, the optimum dilution above the specified limit depends on the operational characteristics of the process rather than on the physicochemical properties of the catalyst.

The properties of catalysts based on rubidium and cesium ferrites were also examined, and a perfect analogy to the formation of the iron–potassium system was found. However, Table 4 indicates that the catalytic activity of the catalysts was dramatically improved when potassium is replaced by rubidium or cesium.

Table 5. Performance characteristics of catalysts based on iron oxides and alkali metals in the processes of ethylbenzene and olefin dehydrogenation

Catalyst	Catalytic characteristics*		Service life, years	Improved parameter
	X, %	*S*, wt %		
Ethylbenzene dehydrogenation				
K-22	60–65	87–88	1.5–2	–
K-24	72	89–90	2	Changes in the chemical composition of catalysts for increasing the concentration of an active component—a solid solution of silicon and chromium in the crystal lattice of potassium ferrite
				Changes in the activation conditions for the ingress of chromium into the lattice of an active component
K-26	75	90	–	Replacement of parent iron oxide with iron–chromium spinel
K-28	72	97	2	Partial replacement of potassium with cesium
Dehydrogenation of *n*-butenes to butadiene				
K-16u	28–30	75–80	–	–
K-24	22–24	82	–	–
K-28	37–40	90–95	–	–

* *X* is the degree of conversion, and *S* is the selectivity for styrene or butadiene, respectively.

The nature of active components in the catalysts based on iron oxides was determined, and the genesis of the phase composition and texture of this catalyst was studied. This made it possible to develop a new K-24 catalyst modification for the dehydrogenation of olefins and ethylbenzene instead of the less active K-22 modification (Table 5). In contrast to the phosphate catalyst, it was necessary to change the chemical composition of the catalyst in this case. These changes were performed to increase the concentration of the active component, a solid solution of silicon and chromium in the crystal lattice of potassium ferrite. To obtain the optimum texture of the catalyst, α-Fe_2O_3 with a specific surface area of 3–4 m^2/g prepared by the thermal decomposition of iron(II) sulfate was recommended. Studies of catalysts containing cesium instead of potassium formed the basis for the development of a new K-28 catalyst. The developed catalyst modifications are superior to previous domestic samples in its catalytic and operational characteristics and are highly competitive with the best world analogs [10].

The improvement of catalysts based on iron oxides was continued by developing a new highly active and selective supported catalyst for the processes of olefin dehydrogenation to dienes [28]. The catalyst consists of alkali metal ferrites supported on a spherical-particle corundum. The active component concentration is 5–10 wt %. Table 6 summarizes the results of laboratory tests of the supported catalyst compared with a bulk catalyst of the same composition. All samples were equal in particle size. It can be seen that the supported catalyst is more active and selective than the bulk catalyst. Commercial corundum from OAO Katalizator was used as a support. The feedstock dilution with steam can significantly be reduced using a spherical supported catalyst.

3.4. Development and Characterization of Supported Bimetallic Catalysts for the Steam Dehydrogenation of Lower Paraffins

We demonstrated in Section 2 that the dehydrogenation of lower paraffins was improved in the last two decades by the use of supported polymetallic platinum systems instead of traditional chromia–alumina catalysts [2, 3, 5, 8, 9, 12–14]. Depending on the process organization, the following two types of supported catalysts are distinguished:

(1) Bimetallic catalysts supported on alumina (γ-Al_2O_3) for the selective dehydrogenation of C_3–C_5 paraffins in a hydrogen atmosphere to produce olefins. A catalyst of this type is used in the UOP Oleflex process [5, 12].

(2) Bimetallic catalysts supported on alumina spinel.

In the catalysts of the second type, both the active component and spinel are highly resistant to steam. Therefore, it became possible to perform the dehydrogenation of paraffins in a steam atmosphere; the partial pressure of hydrocarbons was thus reduced, and the yield of target products was increased. Moreover, steam can serve as a heat-transfer agent to provide the zone of endothermic reaction with heat. It is well known that both chromia–alumina catalysts and platinum–alumina catalysts cannot work in a steam atmosphere, because steam poisons chromium oxide is poisoned and causes alumina support agglomeration.

Considering the above facts, we focused our efforts toward developing a new catalyst for the dehydrogenation of lower paraffins on a bimetallic platinum-containing system supported on spinel [8, 9]. However, we worked on the catalyst for a new single-stage process, which had no precedent at that time, rather than on the catalyst for the STAR process [12, 14]. This new process was the steam dehydrogenation of isopentane to isoprene (or *n*-butane to butadiene) at an atmospheric pressure, which did not require sophisticated vacuum equipment.

The situation that existed in the late 1970s before our studies was paradoxical. Almost all conceivable procedures for the preparation of bimetallic catalysts of this type were patented, and all available elements of the periodic table were recommended for use as modifying additives to supported platinum [2]. At the same time, no theory of the design and preparation of such catalysts was developed.

The physicochemical basis for the preparation of new-generation bimetallic catalysts supported on thermally stable spinel for C_3–C_5 paraffin dehydrogenation was developed is due to studies performed in our laboratory. This made it possible to optimize the composition and working conditions of the catalyst and develop a technology for its production.

Note that the development of a preparation procedure for these catalysts consisted in solving the following two relative problems.

(1) The development of a scientific basis for the synthesis of spinel support with the desired composition and texture characteristics.

Table 6. Catalytic characteristics of supported and bulk catalysts based on alkali metal ferrites in the dehydrogenation reactions of olefins

Catalyst	*T*, °C	H_2O/C_4H_8, mol/mol	Conversion of *n*-butenes, %	Yield of C_4H_6, mol %	Selectivity, mol %
Supported catalyst	580	10	34.8	31.7	91.0
Bulk catalyst	600	10	33.6	29.8	88.6

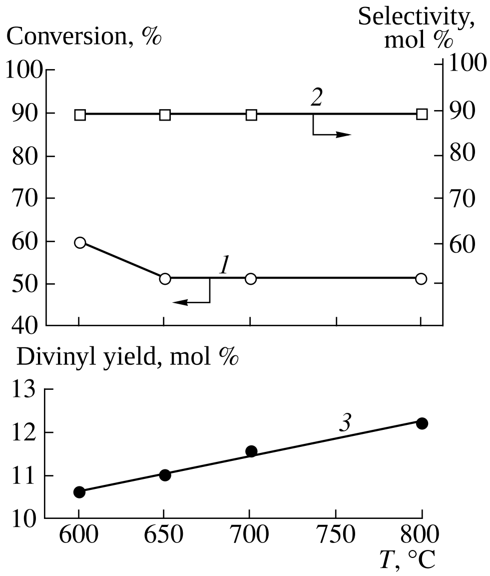

Fig. 1. Effect of calcination temperature on the catalytic properties of a Pt–Sn/$ZnAl_2O_4$ catalyst (0.2 wt % Pt) in the dehydrogenation reaction of *n*-butane: (*1*) conversion, (*2*) selectivity, and (*3*) yield of divinyl.

(2) The development of the synthesis of a supported bimetallic active component with specified composition, structure, and dispersity.

The main results are considered below in this order.

3.4.1. Optimization of the composition and preparation conditions of a spinel support. The use of synthetic alumina spinels as supports for platinum catalysts required solving a number of problems unusual to single-component supports. First, it was necessary to determine the relationships between the properties of supported metal and the nature of a bivalent element incorporated into the spinel support. Second, it was necessary to find the maximum possible concentration of aluminum, zinc, or magnesium oxide unreacted in the course of support synthesis. Finally, it was necessary to determine the optimal crystal structure of the spinel support, which would provide the best properties of the supported catalyst. Because modifying additives dramatically change the properties of platinum, the above questions were addressed in our initial studies of monometallic catalysts supported on the model Zn–Al and Mg–Al materials with different initial oxide ratios. The results were further refined in bimetallic systems.

We found [29, 30] that high catalytic activity and selectivity can be achieved only on platinum supported on the stoichiometric $ZnAl_2O_4$ spinel (the initial ratio $ZnO : Al_2O_3 \approx 1$). When the process is performed in a steam atmosphere, platinum supported on $MgAl_2O_4$ and γ-Al_2O_3 acts as a cracking and complete oxidation catalyst rather than as a dehydrogenation catalyst. The concentration of a free ZnO phase in the Zn–Al support should not be higher than some optimal value, otherwise a side reaction of zinc oxide dissolution in an acid impregnating solution of H_2PtCl_6 occurs at the stage of supporting platinum. This reaction occurs on the support surface and forms zinc hexachloroplatinate ($ZnPtCl_6$) and zinc hydroxide chlorides (ZnOHCl and $Zn_5(OH)_8Cl_2$). The latter substances undergo decomposition in the course of calcination in air and favor the formation of coarse particles of supported platinum [29]. The adverse effect of free ZnO impurities is most pronounced at $ZnO : Al_2O_3 > 1.1$ in the support. Catalysts prepared on a defect Zn–Al spinel ($ZnO : Al_2O_3 < 0.9$) rather rapidly and irreversibly undergo deactivation in the course of operation in a steam atmosphere because of the agglomeration of platinum particles.

An important result is that dispersed Pt particles on the surface of a stoichiometric Zn–Al spinel are highly resistant to agglomeration during activation in oxidizing media. Thus, we found [9] that the catalytic activity of a model Pt/$ZnAl_2O_4$ catalyst remained unchanged as the temperature of calcination in air was increased from 580 to 800°C. Figure 1 demonstrates that a Pt–Sn catalyst supported on the above material exhibited analogous high thermal stability.

It is evident that the high thermal stability of platinum on spinel supports primarily depends on the high thermal stability of the spinel structure and texture. We believe that another reason may be associated with the formation of surface Pt–Zn oxide spinel compounds [9] at the stage of oxidative activation. These compounds are more resistant to thermal dissociation compared with a platinum–alumina complex described in the literature. Highly dispersed metal particles are formed in the course of the subsequent reduction of such surface complexes.

The determination of optimum characteristics of the support allowed us to formulate the requirements to preparation conditions. Thus, in the development of a procedure for preparing the support, it was necessary to attain the maximum yield of the stoichiometric Zn–Al spinel close to 100% while retaining a reasonable specific surface area. Moreover, the prepared support should exhibit a high mechanical strength.

As we expected, the highest yields of spinel at relatively low calcination temperatures (<800°C) were achieved using the coprecipitation of aluminum and zinc hydroxides [30]. The reason is that the components react even at the precipitation stage to form zinc hydroxide aluminates, which decompose on calcination to form spinel. On the other hand, the presence of crystalline hydroxide aluminates in the precipitate impairs the rheological properties of the paste on molding to result in a decrease in the mechanical strength of the pellets. Moreover, the coprecipitation method is characterized by the release of large amounts of wastewater.

A compromise was found in support preparation by mechanically mixing aluminum hydroxide of the pseudoboehmite structure with zinc oxide. To achieve high yields of spinel and to prepare crash-proof pellets, a combination of various factors was required: certain dispersity and morphology of mixed components, a high homogenization degree of systems obtained by mixing under specially chosen conditions, the addition of zinc oxide in a strictly determined small excess to the starting mixture for the complete binding of alumina to spinel, etc. We developed almost waste-free technology for the production of a Zn–Al spinel support with a specified structure and texture characteristics using pseudoboehmite prepared by the hydration of the gibbsite thermal activation product [30].

3.4.2. Determination of the nature of the active component and the optimization of the composition and preparation conditions of the bimetallic catalyst. To determine the optimum composition of a bimetallic catalyst for the dehydrogenation of C_3–C_5 lower paraffins in a hydrogen and steam atmosphere, a series of studies on the nature of an active component and the mechanism of modification by various additives in the Pt–Cu, Pt–Zn, Pt–In, Pt–Sn, and Pt–Pb bimetallic systems supported on spinels was performed [9, 29–33]. It was experimentally found using X-ray diffraction analysis, Moessbauer spectroscopy, high-resolution electron microscopy (HREM), and temperature-programmed reduction (TPR) that alloy particles of platinum with a modifying additive are active components of these catalysts. The dependence of catalytic properties on (a) the chemical composition of supported alloys, which is determined by the nature and concentration of an additive, (b) the crystal structure, and (c) the surface composition was observed. It was found that, compared to pure platinum, solid solutions of a face-centered cubic (fcc) structure with inactive metal concentrations lower than 25 at. % and intermetallic compounds like Pt_3Sn, Pt_3In, etc., exhibit the highest catalytic activity and selectivity in dehydrogenation. Solid solutions with higher concentrations of the second element and alloys with other crystal structures like PtSn, $PtSn_2$, δ-PtZn, PtIn, and PtPb exhibit much lower catalytic activities. The enrichment of an alloy surface with the inactive metal with respect to the bulk composition depends on both the nature of the second component of the alloy and the composition of the gas atmosphere. Therefore, the purposeful selection of a modifying additive and a crystal structure of the alloy depends on the particular reaction conditions of dehydrogenation. Thus, we found that the catalytic activity and selectivity of catalysts containing active fcc alloys in dehydrogenation in a steam or hydrogen atmosphere decreased in the following order:

$$\text{Pt–Sn} > \text{Pt–In} > \text{Pt–Zn} > \text{Pt} > \text{Pt–Cu}.$$

When dehydrogenation on the above catalysts was performed in a hydrogen atmosphere without diluting the feed with steam the activity generally decreased and the process selectivity increased. The order of activity changes:

$$\text{Pt–In} \geq \text{Pt–Sn} > \text{Pt–Cu} > \text{Pt–Zn} > \text{Pt}.$$

This order is almost identical to the published order of activity for bimetallic platinum catalysts supported on γ-Al_2O_3 [34]. However, no data on the nature of an active component were given in [34].

Thus, Pt–Sn catalysts are the most active and selective in steam dehydrogenation, whereas the Pt–In and Pt–Sn systems exhibited the highest activity and selectivity in a hydrogen atmosphere. Table 7 demonstrates that Pt–In catalysts are preferred in the dehydrogenation of isobutane because, when these catalysts are used, side reactions (skeletal isomerization of isobutane to *n*-butane and products of its subsequent dehydrogenation, *n*-butenes, and butadiene) proceed to a smaller extent. Studies on the nature and mechanism of formation of the active component allowed us to develop methods for the preparation of supported bimetallic catalysts with specified composition, structure, and dispersity of an active component for the dehydrogenation of lower paraffins. The reactions of supported components with each other and with the support material were found to be the determining factor in the formation of supported alloys at different stages of catalyst preparation, beginning with the stage of supporting initial components and ending with the stage of operation [9, 30]. We found the main types of such reactions and analyzed their effect on the formation of active fcc alloys. When deciding optimum preparation conditions, the determining factor is the medium in which the catalyst is thermally treated. Thus, the prereduction of dried samples results in the predominant reduction of modified additives to the zero-valence state and in the formation of coarsely dispersed PtSn or PtIn alloys enriched in the inactive metal, which results in catalyst deactivation [30, 31].

Highly active and selective catalysts containing Pt–Sn or Pt–In alloys can be prepared by the reduction of preoxidized samples with a given optimum ratio between the bulk concentrations of components. Alloys can also be formed directly in the course of catalytic reaction under the action of a reaction medium.

The study of the mechanism and other aspects of sorption of platinum compounds and modifying additives on the surface of spinel support [35] allowed us to determine the optimal sequence of operations and conditions of supporting components at the stage of catalyst preparation. This made it possible to obtain an active component in an ultradispersed state with a particle size no greater than 0.5–1 nm, according to HREM data. By increasing the dispersity, the platinum concentration in the prepared Pt–Sn/$ZnAl_2O_4$ catalyst was decreased to 0.15–0.2 wt %.

3.4.3. Optimization of feed dilution with hydrogen and steam. The dilution of paraffin to be dehydrogenated with hydrogen and steam is an important processing step. In this connection, it was necessary to obtain physicochemical grounds for optimum dilution parameters. We found that in dehydrogenation without dilution with hydrogen and steam carbonization occurs by

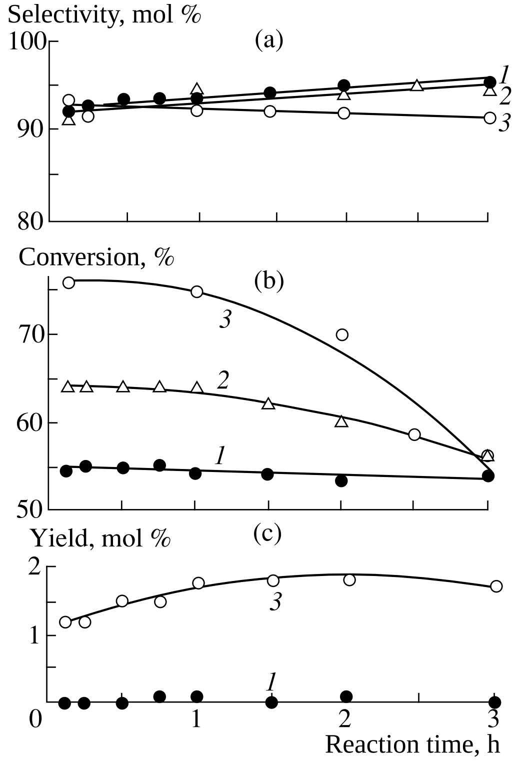

Fig. 2. Effect of the feed dilution with steam on (a) the selectivity for isobutylene, (b) the conversion of isobutane, and (c) the yield of butadiene in the dehydrogenation of isobutane on a Pt–Sn/$ZnAl_2O_4$ catalyst. $H_2O/iso\text{-}C_4H_{10}$: (*1*) 0, (*2*) 10, and (*3*) 20 (T = 575°C; $V_{iso\text{-}C_4H_{10}}$ = 600 h^{-1}; $H_2 : iso\text{-}C_4H_{10} = 1 : 1$).

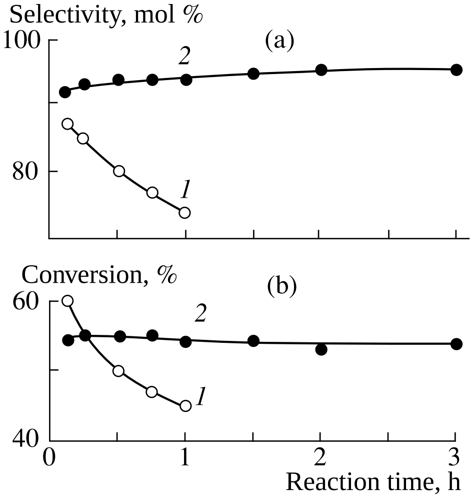

Fig. 3. Effect of the feed dilution with hydrogen on (a) the selectivity for isobutylene and (b) the conversion of isobutane in the dehydrogenation of isobutane on a Pt–Sn/$ZnAl_2O_4$ catalyst. $H_2/iso\text{-}C_4H_{10}$: (*1*) 0 and (*2*) 1 (T = 575°C; $V_{iso\text{-}C_4H_{10}}$ = 600 h^{-1}; $H_2O/iso\text{-}C_4H_{10}$ = 0).

a consecutive mechanism at acid sites of the support and by the mechanism of compensated degradation on the metal particles of an active component. Water vapor was found to almost completely inhibit coke formation on a support because of the oxidation of products formed by consecutive reactions. In contrast to water vapor, hydrogen only slightly affects the carbonization of support but significantly inhibits the carbonization of metal particles. A decrease in the carbonization of an alloy surface in the presence of hydrogen is much more pronounced than that of an unmodified platinum surface. The effect of water vapor on the carbonization of an active component is small compared with that of hydrogen. Because tin additives independently diminish the carbonization of support, the steam concentration in a reaction medium has little effect on a decrease in the rate of catalyst deactivation. In contrast, Figs. 2 and 3 indicate that, at very high dilutions of the feed with steam in the course of isobutane dehydrogenation, the catalyst is gradually deactivated because of an increase in the butadiene concentration in the reaction products (butadiene is the strongest coke-forming agent in comparison with butenes). The role of water vapor in this process is reduced to the partial heat transfer to a reaction zone, as well as to decreasing the partial pressure of hydrocarbons and to increasing the yield of target products. Hydrogen is the most efficient agent that makes it possible to vary broadly the duration of a dehydrogenation cycle. At the same time, the adverse effect of hydrogen on the reaction equilibrium should

Table 7. Effect of the nature of modifying additives on the catalytic properties of platinum in the reaction of isobutane dehydrogenation*

Catalyst	Dilution, mol/mol		Conversion, %	Selectivity, mol %			
	1 : 1	1 : 10		$iso\text{-}C_4H_8$	isomerization**	cracking (C_1–C_3)	oxidation (CO_2 + CO)
Pt–Sn/$ZnAl_2O_4$	H_2	–	54.4	91.7	4.6	3.4	0
	H_2	H_2O	75.7	91.1	2.8	4.3	1.8
Pt–In/$ZnAl_2O_4$	H_2	–	43.9	95.5	0.8	3.4	0
	H_2	H_2O	54.2	94.7	0.3	3.5	1.4

* Reaction conditions: temperature, 575°C; isobutane space velocity, 600 h^{-1}.

** $iso\text{-}C_4H_{10} \longrightarrow n\text{-}C_4H_{10} \longrightarrow n\text{-}C_4H_8 \longrightarrow C_4H_6$.

be considered in the determination of optimal feed dilution with hydrogen.

Generally, the duration of a dehydrogenation cycle between regenerations for the developed Pt–Sn and Pt–In catalysts primarily depends on the quantity of heat that can be supplied to the endothermic reaction zone rather than on the rate of catalyst deactivation due to carbonization. The optimum dilution parameters were determined depending on the nature of the component to be dehydrogenated and on the planned duration of a cycle between regenerations.

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REFERENCES

1. Tyuryaev, I.Ya., *Teoreticheskie osnovy polucheniya butadiena i izoprena metodami degidrirovaniya* (Theoretical Foundation of Butadiene and Isoprene Synthesis by Dehydrogenation), Kiev: Naukova Dumka, 1973.
2. Kotel'nikov, G.R., Strunnikova, L.V., Patanov, V.A., and Arapova, I.P., *Katalizatory degidrirovaniya nizshikh parafinovykh, olefinovykh i alkilaromaticheskikh uglevodorodov* (Catalysts for Dehydrogenation of Lower Akanes, Alkenes, and Alkylaromatic Hydrocarbons), Moscow: TsNIITEneftekhim, 1978.
3. Bursian, N.R. and Kogan, S.B., *Usp. Khim.*, 1989, vol. 58, no. 3, p. 451.
4. Liakumovich, A.G., Mustafin, Kh.V., Akhmed'yanova, R.A., and Khasiulin, M.M., *Ross. Khim. Zh.*, 1999, vol. 43, nos. 3–4, p. 117.
5. Kottrell, P.R., Bakas, S.T., Bentam, M.F., *et al.*, *UOP Technology Conference*, Moscow, 1992.
6. *Neftegaz. Tekhnol.*, 1999, no. 5, p. 70.
7. Gussow, S., *National Petroleum Refiners Association (NPRA) Annual Meeting*, San Antonio, 1991.
8. Kotel'nikov, G.R., Patanov, V.A., Buyanov, R.A., and Bushin, A.N., *Issledovanie i razrabotka tekhnologii proizvodstva monomerov i sinteticheskikh kauchukov* (Research and Development of Technologies of Monomer and Synthetic Rubber Syntheses), Moscow: TsNIITEneftekhim, 1979, no. 3, p. 11.
9. Pakhomov, N.A. and Buyanov, R.A., *Zh. Prikl. Khim.*, 1997, vol. 70, no. 7, p. 1441.
10. Kotelnikov, G.R., *React. Kinet. Catal. Lett.*, 1995, vol. 55, no. 5, p. 537.
11. Sanfilippo, D., Buonomo, F., Fusco, G., *et al.*, *Stud. Surf. Sci. Catal.*, 1998, vol. 119, p. 919.
12. Vora, B.V. and Imai, T., *Hydrocarbon Proc.*, 1982, vol. 61, p. 171.
13. US Patent no. 36700044, 1972.
14. *Oil Gas J.*, 1994, no. 17, p. 50.
15. *Eur. Chem. News*, 1991, vol. 57, p. 1490.
16. *"Isobutene" Hydrocarborn Processing—Computer Analysis of Current HPI Construction., June,* 1991, p. 42.
17. Pakhomov, N.A., Zolotarskii, I.A., and Buyanov, R.A., Abstracts of Papers, *5 Mezhdunarodnaya konferentsya po intensifikatsii neftekhimicheskikh protsessov "Neftekhimiya-99" (5th Int. Conf. on Intensification of Petrochemical Processes),* Nizhnekamsk, 1999, vol. 2, p. 19.
18. Gil'mutdinov, N.R., Khafizov, A.V., Korshunov, A.I., *et al.*, *Nefteper. Neftekhim.*, 1996, no. 9, p. 29.
19. Aminova, L.Z. and Bazhenov, Yu.P., *Proizvod. Isp. Elastomer.*, 1998, no. 1, p. 3.
20. Molchanov, V.V., *Kinet. Katal.*, 1992, vol. 33, no. 4, p. 873.
21. Andrushkevich, M.M., Molchanov, V.V., Kustova, G.N., *et al.*, *Kinet. Katal.*, 1980, vol. 21, no. 4, p. 1034.
22. Andrushkevich, M.M., Kotel'nikov, G.R., Molchanov, V.V., *et al.*, *Kinet. Katal.*, 1980, vol. 21, no. 4, p. 1041.
23. Andrushkevich, M.M., Kotel'nikov, G.R., Molchanov, V.V., *et al.*, *Kinet. Katal.*, 1980, vol. 21, no. 5, p. 1306.
24. Andrushkevich, M.M., Kotel'nikov, G.R., Molchanov, V.V., *et al.*, *Kinet. Katal.*, 1980, vol. 21, no. 5, p. 1321.
25. USSR Inventor's Certificate no. 333796, *Byull. Izobret.*, 1971.
26. Kotel'nikov, G.R., Strunnikova, L.V., Sirotkin, B.V., *et al.*, *Issledovanie i razrabotka tekhnologii proizvodstva monomerov i sinteticheskikh kauchukov* (Research and Development of Technologies of Monomer and Synthetic Rubber Syntheses), Moscow: TsNIITEneftekhim, 1976, no. 2, p. 26.
27. Molchanov, V.V., Plyasova, L.M., and Andrushkevich, M.M., *Kinet. Katal.*, 1991, vol. 32, no. 4, p. 1008.
28. USSR Inventor's Certificate no. 1582401, *Byull. Izobret.*, 1990.
29. Pakhomov, N.A. and Buyanov, R.A., *Adv. Catal.*, 1985, p. 305.
30. Pakhomov, N.A., Buyanov, R.A., and Zolotovskii, B.P., *Stud. Surf. Sci. Catal.*, 1998, vol. 118, p. 185.
31. Pakhomov, N.A., Buyanov, R.A., Yurchenko, E.N., *et al.*, *React. Kinet. Catal. Lett.*, 1980, vol. 14, p. 329.
32. Pakhomov, N.A., Buyanov, R.A., and Moroz, E.M., *Kinet. Katal.*, 1981, vol. 22, no. 2, p. 488.
33. Pakhomov, N.A., Zaitseva, N.A., and Moroz, E.M., *Kinet. Katal.*, 1992, vol. 33, no. 2, p. 426.
34. Luu Cam Loc, Gaidai, N.A., and Kiperman, S.L., *Proc. 9th Int. Congr. on Catalysis*, Canada: Chemical Institute of Canada, 1988, vol. 3, p. 1261.
35. Pakhomov, N.A. and Buyanov, R.A., *Stud. Surf. Sci. Catal.*, 1995, vol. 105, p. 1101.