Reversible and Irreversible Deactivation of Supported Bimetallic Catalysts for the Dehydrogenation of Lower Paraffins

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Abstract—The reasons and nature of the deactivation of spinel-supported bimetallic Pt–Sn, Pt–In, and Pt–Cu catalysts in the steam dehydrogenation of C_4–C_5 paraffins are analyzed. The deactivation can be reversible and irreversible. Reversible deactivation is associated with the effects of the composition of reaction medium and gaseous medium for preliminary treatment on the surface composition of supported bimetallic alloys and with the coking of catalysts. Irreversible deactivation can result from the irreproducibility of the phase composition and dispersion of supported alloys in dehydrogenation–regeneration cycles and from the carbon erosion of catalysts. This erosion consists in the removal of active metal particles to the bulk of carbon deposits. The formation of carbon deposits on the surfaces of spinel supports and bimetallic catalysts is considered. Recommendations for optimizing the composition and the operating conditions of catalysts are given in order to reduce the effects of factors that result in reversible and irreversible deactivation.

INTRODUCTION

Olefins and dienes C_3–C_5 (propylene, *n*-butenes, isobutylene, butadiene, and isoprene) are widely used in the production of synthetic rubber, plastics, high-octane automotive fuel components, and other valuable chemical products. For this reason, there has been considerable interest in the intensification of their production methods within the last half a century, primarily, in the improvement and development of new dehydrogenation catalysts.

Until recently, a chromia–alumina catalyst was considered as the single best catalyst for lower paraffin dehydrogenation. However, although this catalyst exhibits high initial activity and selectivity, it has two considerable disadvantages [1]: (1) it is rapidly deactivated in the course of reaction because of the formation of carbon deposits, and (2) it is easily poisoned by water vapor.

To overcome the former disadvantage, dehydrogenation is performed either in a fixed bed of a catalyst in a batch mode with alternating dehydrogenation and regeneration cycles or in a fluidized bed of a microspherical catalyst, which circulates between a reactor and a regenerator. The latter disadvantage gives no way of using steam as a diluent, which reduces the partial pressure of hydrocarbons and improves the yield of target products. Therefore, the fixed-bed process is performed in a vacuum.

Several dozens of plants using specific modifications of a chromia–alumina catalyst are in operation in the world's industry. However, efforts were repeatedly made to replace this catalyst. The development of supported bimetallic and polymetallic catalysts for lower olefin dehydrogenation may serve as an example of a partial solution to this problem. The idea that these catalytic systems can be used for dehydrogenation processes arose from experience in their applications to gasoline reforming. A platinum–alumina catalyst has been used in reforming since the early 1940s, but it exhibits very low selectivity in the dehydrogenation of lower paraffins compared with a chromia–alumina catalyst. However, the discovery of the modification of a Pt/Al_2O_3 reforming catalyst with rhenium, tin, lead, germanium, indium, and other element additives [2] resulted in the appearance of a great number of patents taken by almost the same companies [3] that recommended supported bimetallic systems of this type for use as dehydrogenation catalysts.

The widespread practical use of supported bimetallic platinum catalysts in reforming processes is explained by the fact that modifying additives considerably improve the characteristics of the supported active metal. The specific activity and selectivity of the metal and the dispersion and thermal stability of supported particles can increase, and the resistance of catalysts to various catalyst poisons, primarily including carbon deposits, is enhanced [4]. The thermal stability of the active component and its resistance to deactivation by carbon deposits is a particularly topical problem in the case of bimetallic catalysts for the dehydrogenation of lower C_3–C_5 paraffins because these catalysts operate under more severe reaction conditions—at high temperatures with alternating oxidative and reductive media. However, the stability of these catalytic systems to deactivation was insufficiently described in the literature.

The following two types of supported bimetallic catalysts are used depending on the organization of a dehydrogenation process:

(1) spherical catalysts on aluminum oxide for the selective dehydrogenation of C_3–C_5 paraffins to olefins in a hydrogen atmosphere and a moving bed [5];

(2) catalysts with alumina spinel carriers, which exhibit high thermal stability [6–8].

In the catalysts of the second type, not only the active component, but also the spinel carrier is highly resistant to the action of water vapor. This fact opens up radically new opportunities for performing the steam dehydrogenation of paraffins in order to reduce the partial pressure of hydrocarbons and to increase the yield of target products. Moreover, steam can serve as a heat-transfer agent to provide heat input to the endothermic reaction zone. In the case of *n*-butane or isopentane dehydrogenation, the corresponding dienes can be prepared in a single step on a catalyst of this type because of a decrease in the partial pressure of hydrocarbons upon feed dilution with steam. Thus, the use of sophisticated vacuum equipment becomes unnecessary. On this basis, a single-step process, which has no analogs the world over, for isopentane dehydrogenation to isoprene at atmospheric pressure was developed at the OAO Yarsintez and the Boreskov Institute of Catalysis (Novosibirsk) [6, 7].

The aim of this work was to summarize our data on the resistance to deactivation of spinel-supported bimetallic Pt–Sn, Pt–In, and Pt–Cu catalysts for the steam dehydrogenation of lower paraffins.

GENERAL PROBLEMS OF THE DEACTIVATION OF SUPPORTED CATALYSTS

To discuss conceivable reasons for the deactivation of supported bimetallic catalysts, let us consider the classification [9], according to which all changes in catalytic properties are subdivided into the following two classes:

(1) changes in the specific activity and selectivity due to changes in the chemical and phase composition in the course of catalyst operation;

(2) changes in the catalyst structure (texture), which are responsible for the loss of catalytic activity as a result of a decrease in the working surface area and its accessibility.

In turn, either of these two classes is subdivided into subgroups in accordance with the specific features of a particular catalyst and its operating conditions. The deactivation of supported monometallic and bimetallic catalysts can result from changes in the chemical and structural properties of both the supported component and the carrier. The first group includes changes in the surface and phase composition of the supported component and the interaction between the active component and the carrier. The second group includes changes in the dispersion of the supported active component; coking; changes in the phase composition of the carrier; and sintering and mechanical degradation of the carrier.
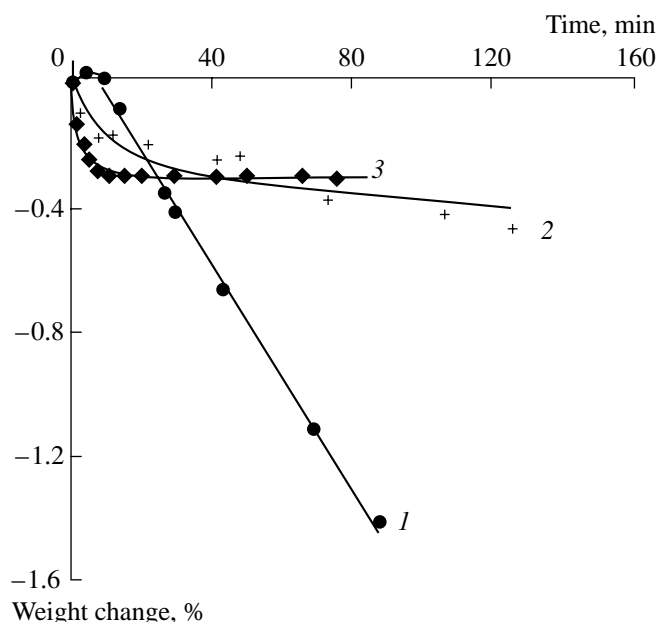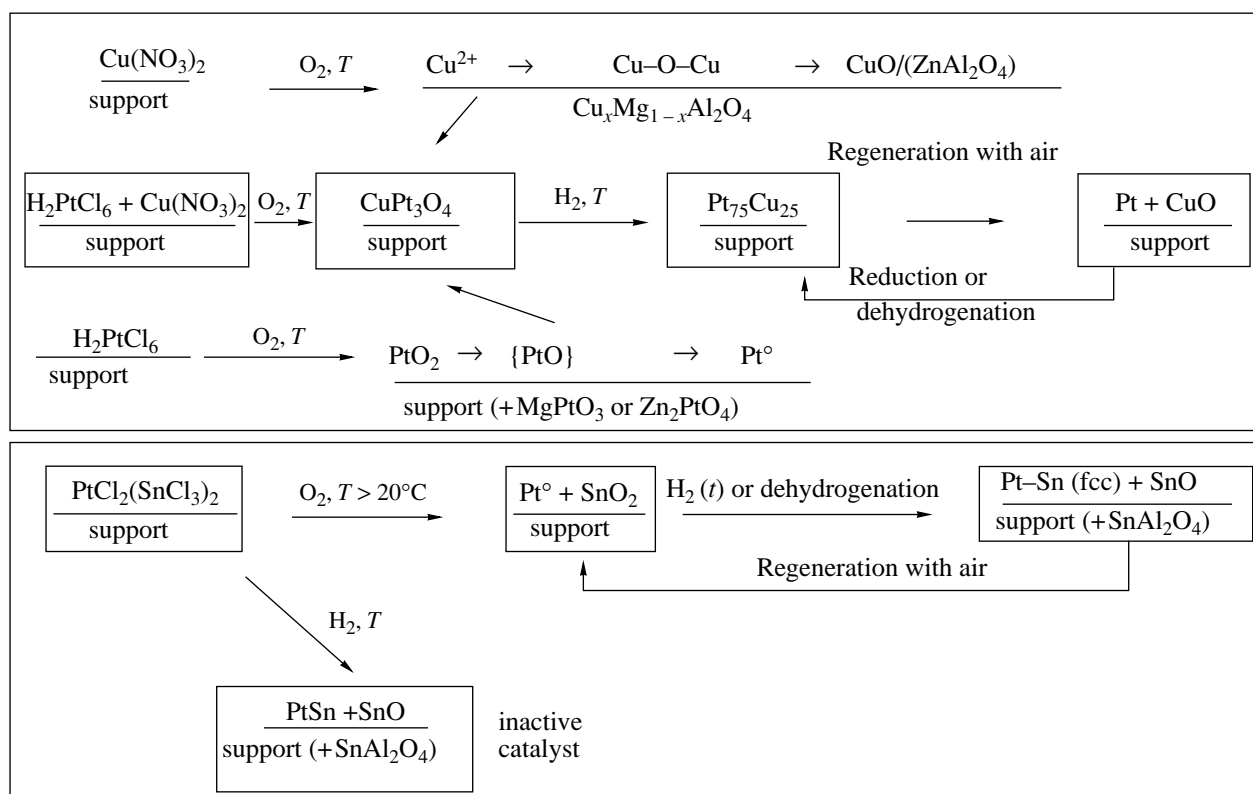

Fig. 1. Changes in the sample weight on the reduction of (*1*) the initial $ZnAl_2O_4$ carrier and (*2*) Pt/$ZnAl_2O_4$ (0.9% Pt) and (*3*) Pt–Sn/$ZnAl_2O_4$ (1.0% Pt; Sn/Pt = 3) catalysts with hydrogen. Conditions of reduction: $T = 580°C$; $H_2 : Ar = 1 : 10$.

Note that spinel carriers are characterized by high thermal stability, and their specific surface area and porous structure remain unchanged in the course of operation. Changes in the carrier phase composition under exposure to a reducing medium would be expected only in the case of Zn–Al spinel because Zn^{2+} cations can be reduced to zinc metal, whereas the carrier based on Mg–Al spinel exhibits high resistance to reduction. As can be seen in Fig. 1 (curve *1*), the weight of the $ZnAl_2O_4$ carrier decreased on the treatment in a hydrogen atmosphere. The deep reduction of this carrier resulted in the degradation of a cubic spinel phase and in its transfer to a corundum phase [10]. However, the reduction of Zn–Al spinel was inhibited in the presence of Pt within the temperature range of a dehydrogenation reaction (Fig. 1, curve *2*). The addition of tin suppressed this process [10]. In the reduction of a Pt–Sn/$ZnAl_2O_4$ catalyst with hydrogen under the same conditions, small weight losses were observed only at the initial moment, and they resulted from the reduction of SnO_2 to Sn^{2+} and Sn^0 (Fig. 1, curve *3*).

The problems of the mechanical strength of spinel supports are beyond the scope of this paper. Note that this strength is somewhat lower than that of aluminum oxide. However, a knowledge of the factors affecting the formation of the phase composition of spinels and their texture at the stage of preparation allowed us to develop a technology for the synthesis of spinels with reasonable mechanical strengths [11].

The resistance of supported catalysts to deactivation significantly depends on the properties of a supported active component. Therefore, let us briefly consider the

$$\frac{Cu(NO_3)_2}{support} \xrightarrow{O_2,\,T} Cu^{2+} \rightarrow \underset{Cu_xMg_{1-x}Al_2O_4}{Cu-O-Cu} \rightarrow CuO/(ZnAl_2O_4)$$

Regeneration with air

$$\frac{H_2PtCl_6 + Cu(NO_3)_2}{support} \xrightarrow{O_2,\,T} \frac{CuPt_3O_4}{support} \xrightarrow{H_2,\,T} \frac{Pt_{75}Cu_{25}}{support} \longrightarrow \frac{Pt + CuO}{support}$$

Reduction or dehydrogenation

$$\frac{H_2PtCl_6}{support} \xrightarrow{O_2,\,T} \underset{support\,(+MgPtO_3\text{ or }Zn_2PtO_4)}{PtO_2 \rightarrow \{PtO\} \rightarrow Pt^{\circ}}$$

$$\frac{PtCl_2(SnCl_3)_2}{support} \xrightarrow{O_2,\,T>20^{\circ}C} \frac{Pt^{\circ} + SnO_2}{support} \xrightarrow{H_2\,(t)\text{ or dehydrogenation}} \frac{Pt\text{–}Sn\,(fcc) + SnO}{support\,(+SnAl_2O_4)}$$

Regeneration with air

$$\xrightarrow{H_2,\,T} \frac{PtSn + SnO}{support\,(+SnAl_2O_4)} \quad \text{inactive catalyst}$$

Scheme 1. The genesis of spinel-supported Pt–Cu and Pt–Sn catalysts in the course of thermal treatment in different media [7, 11–16]. Support: $ZnAl_2O_4$ or $MgAl_2O_4$.

nature of this component in bimetallic dehydrogenation catalysts and dwell on changes in their phase and surface compositions depending on the compositions of reaction and pretreatment media and on process conditions.

NATURE OF AN ACTIVE COMPONENT IN SUPPORTED BIMETALLIC CATALYSTS

Both published data and our experimental results suggest that alloy particles are the active components of supported platinum catalysts modified with the additives of readily reducible Group I–IV elements (Cu, Zn, In, Sn, and Pb) [4, 7, 10–19]. It is likely that we pioneered the use of direct X-ray diffraction analysis for detecting the formation of tin solid solutions in platinum in the Pt–Sn/$ZnAl_2O_4$ catalyst under exposure to a reaction medium [13].

Changes in the catalytic properties of bulk and supported alloys are usually explained by the effects of two factors—geometric and electronic [4, 20]. However, only the fact of the formation of a supported alloy was mentioned in many publications, whereas changes in the crystal structure of the active metal escaped notice. At the same time, it is well known [21] that platinum can form a continuous series of solid solutions with some elements (Cu, Ir, and Re) with the retention of the initial face-centered cubic (fcc) lat-

tice, whereas other elements (Sn, Zn, Pb, In, etc.) are restrictedly soluble in platinum. In the latter case, intermetallic compounds of different compositions and structures can be formed.

Previously [7, 12, 15], fcc solid solutions with inactive metal concentrations below 25 at. % and intermetallic compounds like Pt_3Sn, Pt_3Zn, and Pt_3In were found to exhibit the highest catalytic activity and selectivity in the steam dehydrogenation of butane and isopentane. The Pt–Cu solid solutions with higher copper contents and alloys with other crystal structures (PtSn, δ-PtZn, PtIn, and PtPb) exhibit much lower catalytic activity.

Formation of Supported Alloys in the Course of Preparation and Operation of Bimetallic Catalysts

Previously [7, 11–16], the formation of various alloys on spinel supports was studied in detail. The results of these studies are schematically represented using the Pt–Cu and Pt–Sn systems as examples.

In analysis of the above data, several important aspects should be taken into consideration. First, note that the right choice of a medium for the thermal treatment of catalysts is a crucial factor in deciding on optimum preparation conditions for bimetallic catalysts. As

shown in the scheme, the pretreatment of dried Pt–Sn samples with hydrogen primarily results in the reduction of modifying additives to a zero-valent state and in the formation of the PtSn alloy. This results in almost complete and irreversible deactivation of the catalyst. Highly active and selective catalysts containing active alloys can be prepared only by the oxidative thermal treatment (activation) and subsequent reductive treatment of samples with a specified ratio between components. Alloys can be formed directly in the course of a catalytic reaction under exposure to the reaction medium [7, 11].

Second, the formation of surface and bulk Pt–Zn or Pt–Mg oxide spinel compounds [7, 12], which are highly stable to thermal dissociation, at the stage of oxidative activation is a very interesting property of catalysts supported on spinels. In our opinion, this stabilization of platinum in an oxide state on the stoichiometric Zn–Al spinel surface, along with the high thermal stability of the structure and texture of spinels, is primarily responsible for an increase in the stability of disperse particles of the active metal to sintering in the activation in oxidative media. It was found [7] that the catalytic activity of the $Pt/ZnAl_2O_4$ model catalyst remained unchanged as the temperature of its calcination in air was increased from 580 to 800°C. The activity of the $Pt/MgAl_2O_4$ catalyst began to decrease at temperatures higher than 700°C [12]. On the other hand, it is well known that platinum on alumina began to agglomerate on calcination in air at temperatures higher than 600°C, that is, simultaneously with the decomposition of a surface platinum–aluminum oxide complex [22, 23]. The $Pt–Sn/ZnAl_2O_4$ catalyst also exhibits high thermal stability [24]. However, the unique ability of spinel to stabilize the disperse state of supported particles completely manifests itself in the oxidative activation of Pt–Sn samples prepared by the successive deposition of platinum on a Sn-containing spinel carrier. The preparation of catalysts by coimpregnation with the use of Pt–Sn complex solutions results in a partial loss of the stabilizing effect of spinels. This results from the genesis of supported complexes. They are prone to redox degradation in contact with air in the course of drying and calcination with the formation of platinum metal particles and tin dioxide [15], which prevents the formation of Pt–Zn oxide compounds.

It is likely that an increase in the dispersion of supported particles of a metal phase due to its stabilization in an oxidized state at the stage of thermal treatment is a general phenomenon. As shown in the scheme, a competitive reaction of the formation of the $CuPt_3O_6$ compound and (or) the $Cu_{1-x}Pt_xO$ ($x = 0.135–0.355$) solid solution occurs in parallel with the interaction of copper and platinum with the carrier in the calcination of a bimetallic Pt–Cu catalyst prepared by coimpregnation [16]. This facilitates a dramatic decrease in the particle size of a Pt–Cu alloy formed in the course of subsequent reduction of the samples. However, according to the data of X-ray diffraction analysis and Moessbauer spectroscopy, the interaction between platinum and tin in an oxide state does not take place in the Pt–Sn system [15]. For this reason, the size of supported metal particles was changed insignificantly as the tin content of catalysts prepared by deposition from the solutions of Pt–Sn complexes increased.

Finally, alloy particles show a tendency to bulk and surface segregation [25, 26], and this is one of the most important properties of supported bimetallic catalysts, which is primarily responsible for their performance characteristics. The bulk segregation consists in the degradation of alloys, which are formed under exposure to a reducing medium (the reaction medium can also play this role), to release platinum metal particles and oxides of the additive in the course of oxidative treatment. Because the activity of bimetallic catalysts deceases in the course of lower paraffin dehydrogenation as a result of carbon deposition, the catalysts should be subjected to oxidative regeneration. In the above scheme, this cyclic alternation of oxidizing and reducing media is represented as a reversible cycle in which the phase composition of the catalyst is changed. In principle, this procedure should provide the retention of its initial activity. Indeed, in actual practice, the best samples of $Pt–Sn/ZnAl_2O_4$ catalysts can withstand a great number of dehydrogenation–regeneration cycles. However, because alloys are unstable in an oxidizing atmosphere, the gradual activity loss due to the irreproducibility of the alloy composition in a regular cycle of dehydrogenation is always a problem. Evidently, the coking of catalysts should be prevented or diminished because the possibility of alloy degradation cannot be excluded on carbon burning. The realizability of this prevention for the given systems will be considered below. Here, it should only be noted that the lower the degree of catalyst coking, the lower the risk of irreversible deactivation. We performed special experiments under conditions of intense coking accompanied by a rapid loss of the activity or with the accumulation of a large amount of coke and a slow decrease in the activity. We found that a catalyst can undergo dramatic changes under these conditions. Finally, these changes result in the irreversible deactivation of the catalyst. As will be demonstrated below, carbon erosion, which manifests itself in the removal of active particles to the bulk of carbon deposits with a simultaneous decrease in their dispersion, is among the causes of irreversible deactivation. The second cause is an excessive accumulation of carbon deposits, which can result in catalyst overheating in the course of regeneration and, as a consequence, in considerable phase separation in the bimetallic system. This makes the system incapable of forming an active alloy of the same composition and with the same dispersion in a new cycle of dehydrogenation.
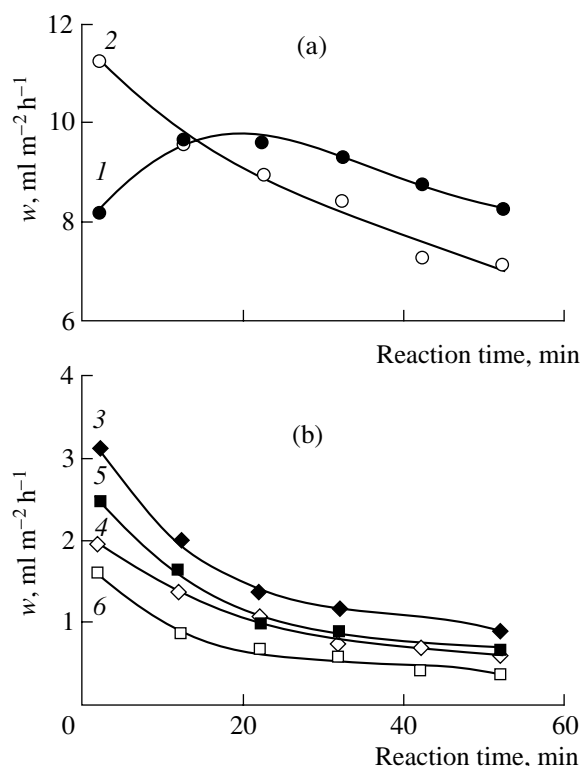
Fig. 2. Dependence of the rates of isopentane (*1*, *2*) dehydrogenation, (*3*, *4*) cracking, and (*5*, *6*) deep oxidation with steam on the reaction time on (*2*, *4*, *6*) oxidized and (*1*, *3*, *5*) additionally reduced Pt–Sn/ZnAl$_2$O$_4$ catalysts. Catalyst composition: Pt, 0.56 wt %; Sn, 0.45 wt %. Reaction conditions: $T = 582$°C; i-C$_5$H$_{12}$: H$_2$: H$_2$O = 1 : 1 : 10; space velocity, $v_{i = C_5H_{12}} = 225$ h^{-1}. Conditions of reduction: $T = 580$°C; time, 1 h.

Effects of the Reaction Medium and the Pretreatment Medium on the Properties of Supported Catalysts

The surface segregation of alloys results in a considerable difference in the bulk and surface composition [25, 26]. The surface enrichment with an alloy component depends on the nature of these components, the treatment temperature, and the composition of a gas medium. In a vacuum, the surface is enriched in a metal with a lower heat of sublimation or with a lower melting temperature. As for the bimetallic systems under consideration, their surface in a vacuum is enriched in an inactive metal modifier. The surface enrichment with a particular component in a gas medium depends on the chemical affinity of the gas to either of the two alloy components. In this context, the dehydrogenation of lower paraffins is a very convenient model reaction for studying the effects of surface segregation because the process can be performed either in a purely reductive medium or on diluting the feed with steam. In the former case, the enrichment of alloy surfaces with platinum should be expected. It is likely that this enrichment is responsible for a noticeable increase in the dehydrogenation activity on PtSn-type alloys in a pure

hydrogen atmosphere [7, 11]. In this case, the surface composition approaches that of fcc alloys. In the presence of steam, which can play the role of an oxidizing agent, the surface can be enriched in an inactive metal, which forms a surface oxide [26]. Therefore, the PtSn alloy completely loses its activity. Evidently, the δ-PtZn, PtIn, and PtPb alloys are inactive in a water vapor medium for the same reason.

The effect of the reaction medium on fcc alloys depends on the nature of a modifying element. Thus, a solid solution of tin in platinum and the Pt$_3$Sn alloy exhibit comparatively low sensitivity to steam exposure. Because of this, the Pt–Sn catalyst can be used in the single-step process of paraffin dehydrogenation to dienes [6, 7, 11]. The catalytic activity and selectivity of Pt–Cu solid solutions decrease on feed dilution with steam. The higher the copper content of the alloy, the more sensitive the system to the poisoning effect of steam [16]. In steam dehydrogenation, catalysts containing Pt–In solid solutions are highly selective in cracking and deep oxidation reactions [7].

In general, the catalytic activity and selectivity of catalysts containing fcc alloys in dehydrogenation in a steam and hydrogen medium decrease in the order

Pt–Sn > Pt–In > Pt–Zn > Pt > Pt–Cu.
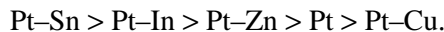
If the process is performed in a hydrogen medium, the overall conversion decreases, and the selectivity increases, whereas the order of activity undergoes considerable changes:

Pt–In ≥ Pt–Sn > Pt–Cu > Pt–Zn > Pt.
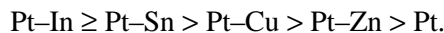
The effect of surface segregation in supported fcc alloys can also be explained by the experimentally observed dependence of the catalytic properties of a Pt−Sn catalyst on the composition of a pretreatment medium. Figure 2 illustrates the effect of additional reduction (before measuring the catalytic activity) of an oxidized (or regenerated) sample on the rate of isopentane dehydrogenation in a water vapor medium. The experiments were performed in a gradientless flow reactor according to the published procedure [27]. It can be seen (Fig. 2, curve *1*) that the preliminary treatment in a hydrogen atmosphere dramatically decreased the initial activity of the catalyst in dehydrogenation and simultaneously increased the activity in side reactions of cracking and deep oxidation with steam. In other words, the pretreatment with hydrogen decreased the selectivity for dehydrogenation products. The oxidized sample, which was not subjected to additional reduction, exhibited a higher initial activity in the target reaction (curve *2*) and a lower activity in side reactions (curves *4*, *6*). It is believed that, in the reduction of the sample in hydrogen, the surface of the Pt–Sn alloy, which was formed before the contact of the sample with the reaction medium, was enriched in platinum. As mentioned above, pure unmodified platinum exhibits very low selectivity in the target reaction of dehydrogenation. The surface composition of a Pt–Sn solid solu-

tion is subsequently changed under exposure to steam, which is a constituent of the reaction medium. The activity of the catalyst in dehydrogenation increases because of an increase in the modifying effect of tin atoms. The rate of dehydrogenation is an extremum function of reaction time because a side reaction of coke formation occurs.

Note that all changes in the catalytic properties depending on the compositions of a reaction medium and a pretreatment medium, which can be relevant to the surface segregation of alloys, are reversible.

CARBON DEPOSITION ON SUPPORTED BIMETALLIC CATALYSTS

The deactivation of catalysts due to the formation of carbon deposits is considered conditionally reversible [9]. However, carbon deposition may also result in irreversible deactivation. The generalities of carbon deposition on the surfaces of spinel supports and bimetallic active components will be considered below, and recommendations for optimizing the catalyst composition and operating conditions in order to diminish the effect of coking will be given.

A butadiene–argon mixture was used for the carbonization of samples. The process was performed in a gradientless flow reactor with a McBain sorption balance. The carbonization curves (Fig. 3, curve *1*) of the starting Zn–Al support exhibit two clearly defined portions: an initial portion with a rapid increase in the sample weight and a steady-state portion with a low rate of carbonization. It is likely that the latter portion results from in layers carbonization, when coke formed at the initial stage begins to catalyze the carbonization process. According to high-resolution electron micrographs (Fig. 4) and the results of X-ray diffraction and chemical analysis, carbon deposits on the surface of Zn–Al spinel are constituted of an amorphous graphite phase, which is almost free of hydrogen. This phase is formed as films, which uniformly cover the support surface, and as plates with insular phase distribution. If tin additives are supported on the surface of spinel by impregnation with tin(II) chloride followed by the conversion into SnO_2 on calcination in air, the carbonization of the support is dramatically inhibited (Fig. 3, curves *2–4*). Supported indium and lithium additives have a similar inhibition effect on the carbonization of the support. The effect of tin on the carbonization of the support considerably depends not only on the tin content but also on the deposition procedure. Thus, tin did not inhibit the carbonization of a support if it was added to the support at the stage of preparation, for example, at the stage of mechanical mixing of powdered initial support components before the step of spinel formation (Fig. 3, curve *5*).

In the monometallic $Pt/ZnAl_2O_4$ catalyst, carbon deposits are formed on the surfaces of both the support and platinum. The carbon erosion of the catalyst occurs
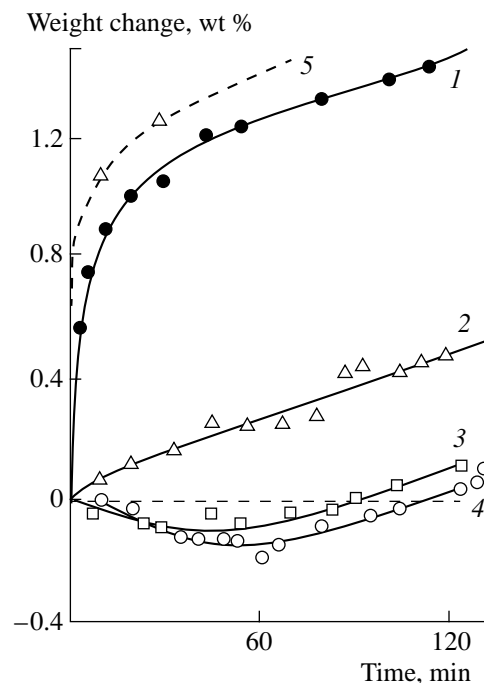


Fig. 3. Effects of the tin content and the procedure of tin deposition on changes in the sample weight in the carbonization of the $ZnAl_2O_4$ carrier: (*1*) initial carrier; (*2–4*) impregnation with a $SnCl_2$ solution at a Sn concentration of (*2*) 0.20, (*3*) 0.52, or (*4*) 3.5 wt %; (*5*) introduction of tin at the stage of carrier synthesis (Sn content of 0.7 wt %).
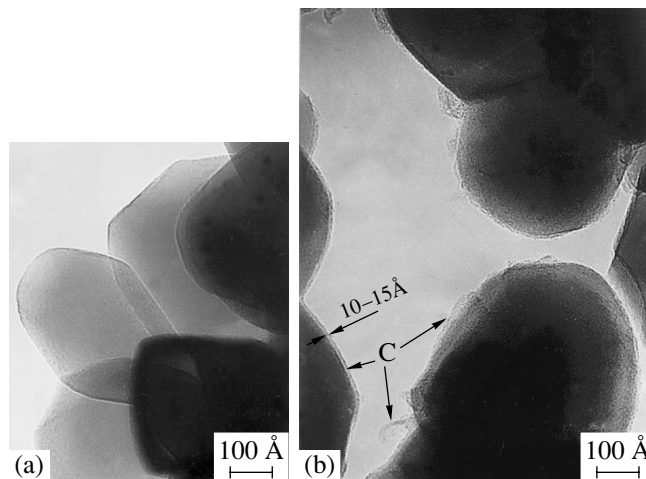
Fig. 4. Electron micrographs of (a) initial and (b) carbonized $ZnAl_2O_4$ carriers. Carbonization conditions: $T = 580°C$; $C_4H_6 : Ar = 1 : 10$; time, 2 h.

in the carbonization in a divinyl medium. This phenomenon is most pronounced in the carbonization of highly dispersed catalysts prepared by the adsorption of platinum from an H_2PtCl_6 solution on the surface of an unmodified Zn–Al spinel carrier or a carrier with tin additives introduced before the stage of spinel formation. Figure 5 demonstrates that in the catalyst after car-
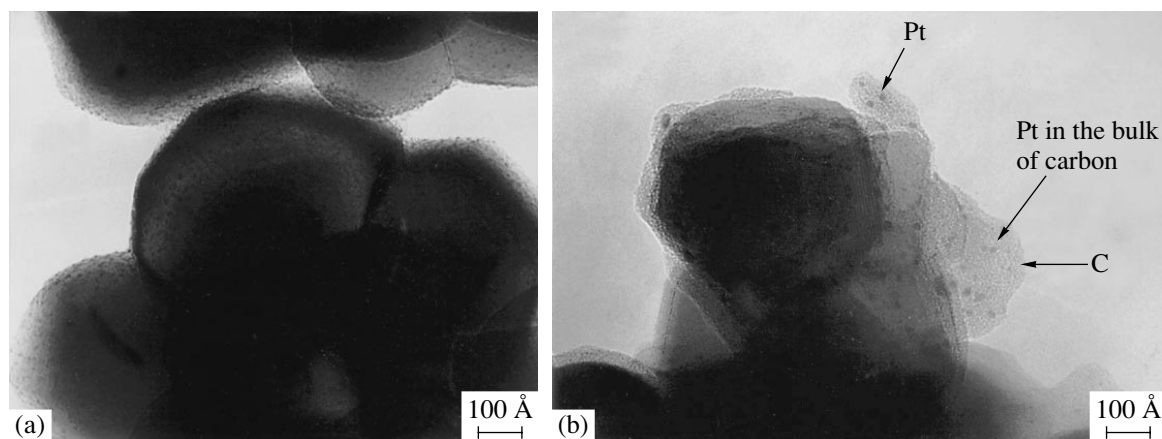
Fig. 5. Electron micrographs of (a) initial and (b) carbonized Pt/ZnAl$_2$O$_4$ catalysts (0.89% Pt). Carbonization conditions are specified in Fig. 4.

bonization metal particles are present in the bulk of the carbon material. The particle size is greater by a factor of two to three than that in the initial sample. As mentioned above, this catalyst did not regain its initial activity after regeneration. Of course, the specified conditions of carbonization are extremely severe, and they do not occur in actual practice. However, the above example illustrates a potential risk that may be associated with dehydrogenation under conditions responsible for the formation of large amounts of carbon in the catalyst.

Tin additives exhibit a complicated effect on the carbonization of the Pt–Sn catalyst. This is due to the fact that tin, as shown in the above scheme, is present in the
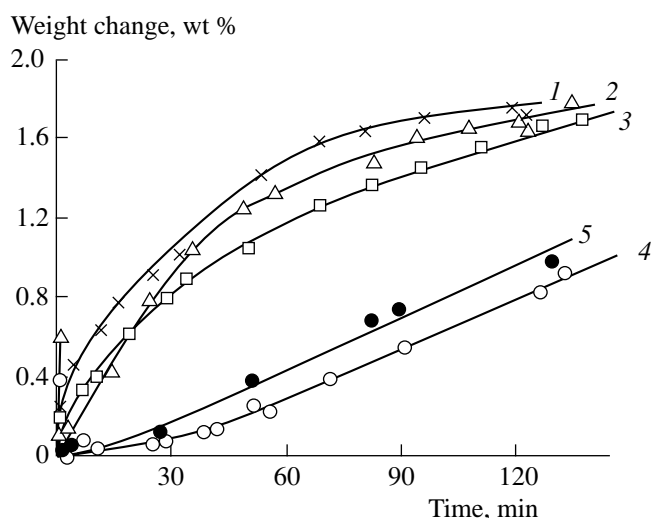
Fig. 6. Effect of the Sn/Pt ratio on the carbonization of calcined Pt–Sn/ZnAl$_2$O$_4$ catalyst samples prepared by coimpregnation from solutions of Pt–Sn complexes: (*1*) 0.59 wt % Pt (Sn/Pt = 2.8), (*2*) 0.50 wt % Pt (Sn/Pt = 1.6), (*3*) 0.45 wt % Pt (Sn/Pt = 3.5), (*4*) 0.42 wt % Pt (Sn/Pt = 6.0), (*5*) sample *4* after reduction with hydrogen for 1 h. Carbonization conditions: T = 580°C; C$_4$H$_6$: Ar = 1 : 10.

catalyst in the two different states: as Pt–Sn alloy particles and as dispersed oxide particles distributed over the surface. As mentioned, tin inhibits centers responsible for the carbonization of the support. At the same time, tin alloyed with platinum can increase or decrease the activity of the catalyst in carbonization depending on the alloy composition. Curves shown in Fig. 6 indicate that samples with the Sn/Pt ratios from 1 to 3 are carbonized to the highest extent, and a further increase in the tin content results in a decrease in the catalyst carbonization. A similar curve with an extremum was also observed in the main reaction of dehydrogenation. As demonstrated previously [12], within the above range of Sn/Pt ratios, the initial conversion of *n*-butane and the yield of divinyl reached maximum values. In this case, a high rate of deactivation is typical of the most active samples. The Pt–In/ZnAl$_2$O$_4$ catalyst exhibited a similar behavior in the dehydrogenation of *n*-butane (Fig. 7). It can be seen that samples with the ratio In/Pt > 4 exhibited the most stable catalytic activity. The smallest amount of coke was formed on the same samples.
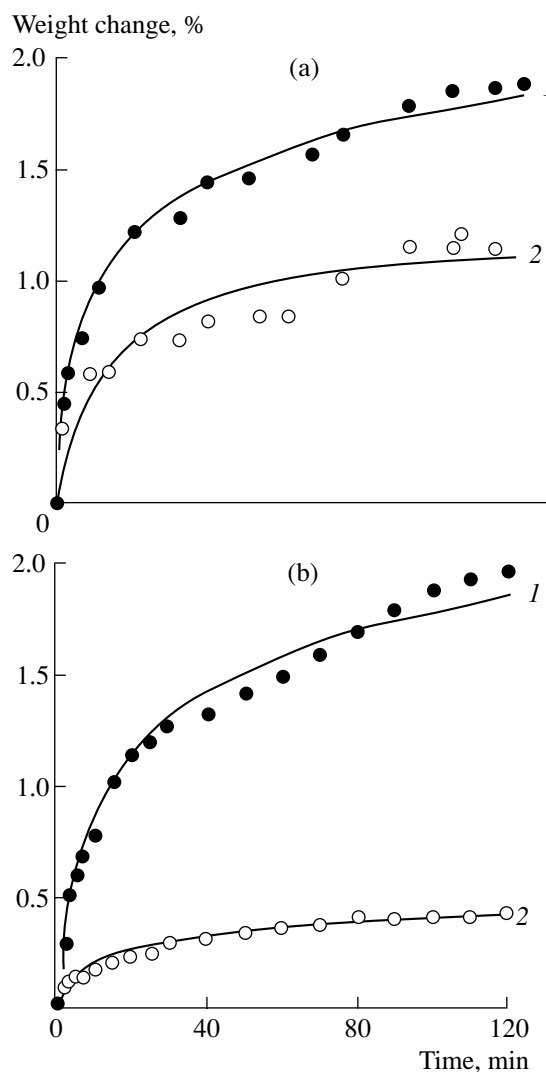
The dilution of dehydrogenated paraffin with hydrogen and steam is an important technological procedure. In this context, the physicochemical justification of optimum dilution parameters seems topical. The kinetic data on carbonization (Fig. 8) and the thermogravimetric analysis of carbonized samples (Fig. 9) suggest that steam almost completely prevents the formation of carbon deposits on the surface of spinel carriers. Hydrogen affects the carbonization of the carrier to a smaller extent than steam does; however, it significantly inhibits the carbonization of metal particles. In this case, hydrogen much more efficiently diminishes the carbonization of the Pt–Sn alloy surface than the carbonization of unmodified platinum (Figs. 8, 9). Similar results were also obtained for Pt–In samples. This fact indicates that the hydrogenation of carbon deposits
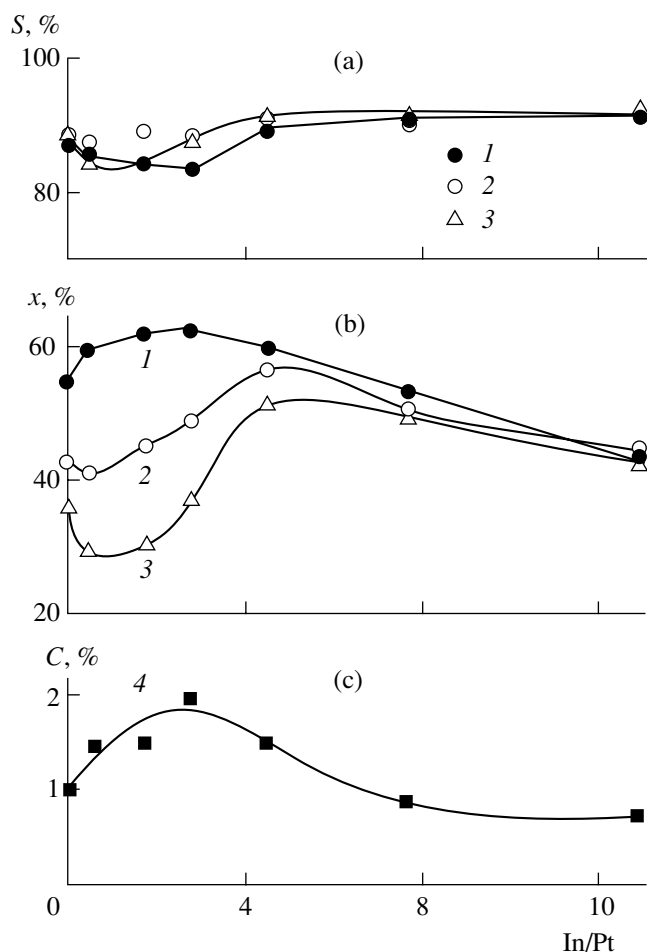
Fig. 7. Effect of the In/Pt atomic ratio on (a) the selectivity of reaction, (b) the conversion of *n*-butane, and (c) the amount of coke deposited for 60 min in the dehydrogenation of *n*-butane on a Pt–In/ZnAl$_2$O$_4$ catalyst (0.55% Pt) at the reaction time of (*1*) 5, (*2*) 30, or (*3*) 60 min. Reaction conditions: T = 575°C; space velocity, $v_{n\text{-}C_4H_{10}}$ = 600 h^{-1}; C$_4$H$_{10}$: H$_2$ = 1 : 0.25.

Fig. 8. Effect of hydrogen on the carbonization of (a) Pt/ZnAl$_2$O$_4$ (0.9% Pt) and (b) Pt–Sn/ZnAl$_2$O$_4$ (1.0% Pt; Sn/Pt = 1.5) catalysts at 580°C: (*1*) C$_4$H$_6$: Ar = 1 : 10 and (*2*) C$_4$H$_6$: H$_2$: Ar = 1 : 1 : 9.

or their precursors on Pt–Sn and Pt–In alloys is intensified in the presence of hydrogen. The higher the content of a modifying element, the more pronounced the hydrogenating effect of the additive.

The effect of steam on the carbonization of the active component is small as compared with the effect of hydrogen (Fig. 9). In general, the steam concentration in the reaction medium has an insignificant effect on the rate of catalyst deactivation [12, 27]. However, the catalyst was gradually deactivated at very high dilution of the feed with steam in the course of isobutane dehydrogenation. This is due to an increase in the concentration of divinyl, which is a stronger coke-forming agent than butenes, in reaction products [24]. The role of steam in the dehydrogenation of C$_4$–C$_5$ paraffin hydrocarbons is reduced to a decrease in the partial

pressure of hydrocarbons and to an increase in the yield of target products. In part, steam also provides heat input to the reaction zone. Hydrogen is the most effective agent, which can dramatically increase the duration of a dehydrogenation cycle in combination with the optimization of the concentration of a modifying additive. At the same time, the adverse effect of hydrogen on the reaction equilibrium should be taken into account in deciding on optimum feed dilution with hydrogen.

In general, the heat input to the zone of an endothermic reaction rather than the rate of catalyst deactivation by carbon deposits is primarily responsible for the duration of a dehydrogenation period between regener-
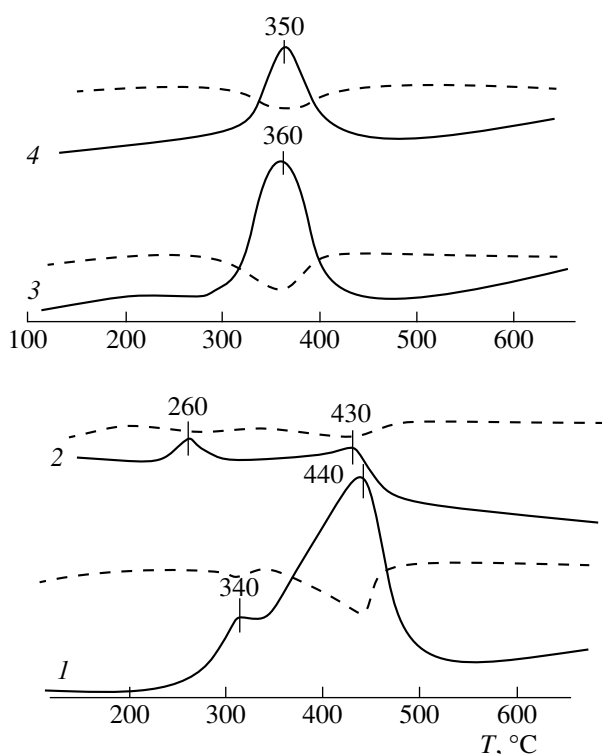
Fig. 9. Thermal analysis curves for the burning of carbon deposits on a Pt–Sn/ZnAl$_2$O$_4$ catalyst (1.1% Pt; Sn/Pt = 3.3) carbonized in different atmospheres: (*1*) C$_4$H$_6$: Ar = 1 : 10, (*2*) C$_4$H$_6$: H$_2$: Ar = 1 : 1 : 9, (*3*) *n*-C$_4$H$_{10}$, and (*4*) *n*-C$_4$H$_{10}$: H$_2$O = 1 : 10. Concentration of C, wt %: (*1*) 2.0, (*2*) 0.25, (*3*) 1.6, and (*4*) 0.8. Solid and dashed lines show DTA and DTG curves, respectively.

ations of Pt–Sn and Pt–In catalysts supported on spinels.

CONCLUSIONS

The reversible and irreversible deactivation of bimetallic catalysts for the dehydrogenation of C$_4$–C$_5$ paraffins, as well as the reasons for this deactivation and the methods for its preventing, can be briefly characterized as described below.

I. Reversible Deactivation:

(1) The alloy surface is enriched in platinum to result in a decrease in the selectivity. The main cause is the inadequate choice of the medium in the preliminary treatment of the catalyst.

(2) The activity and selectivity are impaired because the surface is enriched in an inactive metal in a water vapor medium as a result of the inadequate choice of a modifying additive for given process conditions.

(3) The carbonization of catalysts is an inevitable phenomenon, which can be controlled by changing the nature and content of additives and by diluting the feed with hydrogen.

II. Irreversible Deactivation:

(1) Irreversible deactivation is a consequence of the irreproducibility of the phase composition and dispersion of supported alloys in dehydrogenation–regeneration cycles. It is associated with the carbonization of catalysts and the necessity of oxidative regeneration. Irreversible deactivation can appear at a high degree of catalyst carbonization.

(2) Carbon erosion can occur in the process performed under conditions of intense carbon deposition.

(3) The formation of inactive alloys at the stage of preparation results from the inadequate choice of the medium in the preliminary treatment of the catalyst.

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