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Types of active sites and deactivation features of promoted Pt catalysts for isobutane dehydrogenation

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Abstract

The study is aimed to gain understanding on the mechanism in which Sn and In promoters influence the catalyst deactivation in the course of isobutane dehydrogenation over alumina-supported Pt catalysts. A reaction scheme is postulated envisaging three types of active sites, differing by configuration, adsorption ability, contribution to the reaction routes and vulnerability by coke formations. The model relates the conditions determining the stepwise character of catalyst deactivation earlier observed with the surface fractions of acting types of sites. The approach suggests associating the kinetics of coke formation with the types of sites engaged in the structure of coke precursors.

Keywords: Pt catalysts; Promoter action; Dehydrogenation kinetics; Selectivity; Deactivation

1. Introduction

Detailed knowledge on the behavior of catalytic systems in which more than one type of active sites participate in the reaction mechanism is a subject of both academic and manufacture interest. In the majority of cases the distinct types of active sites differ in adsorption ability. This state of things is of special significance for those catalytic reactions in which the surface concentrations of intermediate species play a key role for the impact of reaction pathways generating by-products and/or carbon formations. In most cases, the reactivity of surface intermediates depends on the strength of their bonds with the catalyst surface. Tight bonds between the catalyst surface and the intermediates favor the generation of coke precursors. In view of this, it is natural to expect that in those cases when more than one type of sites participates in the reaction mechanism, the selectivity and the deactivation pattern would be susceptible to any changes concerning the quantity or the adsorption properties of the different sites.

It has been widely recognized that more than one type of active sites can be distinguished regarding the performance of supported platinum catalysts used for dehydrogenation and refining reactions. Promoting of the active phase with catalytically inactive metals such as Re, In, Ir and Sn is applied in view of increasing the catalyst activity, improving the selectivity and prolonging the catalyst lifetime. The introduction of promoters in the catalyst systems enhances the effects provoked by the diversities in the behavior of the sites facilitating different routes of the processes. Various aspects of the related phenomena are focusing the interest of researchers.

Currently, there is no unique vision in literature, whether ensemble or ligand effects provoked by the presence of promoters play the dominating role for the observed phenomena of changing the catalyst behavior. Different investigators present serious considerations in favor of each of the hypotheses. On the one hand, it is believed that diluting the entities of Pt surface atoms by Sn makes for weaker adsorption affinity, due to modifications in the electron density of Pt [1–4]. Conclusive evidences are presented in literature (e.g., refs. [5–8]) that the addition of Sn affects the stronger sites and decreases the interaction of H_2, CO and C_2H_2 with the catalyst surface. It should be not skipped from consideration, however, that the effect of tin on Pt electron density depends as well on the particle size of the catalytic clusters [4]. At the same time, it gains support the viewpoint noted first by Sinfelt [9] that the geometric factors play a crucial role in cases when the reaction requires active sites consisting of a number of adjacent active metal atoms in a proper configuration. Evidence is reported in literature that the introduction of Sn influences the Pt dispersion [8–18]. The IR experiments of CO adsorption gave evidences both of dilution and electronic effects on Pt by Sn.

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Altogether, lots of the problems seem to be linked to the problem of the nature of active sites participating in the various reactions occurring on the bi-metallic catalysts.

It has been widely recognized that different number of contiguous surface Pt atoms are necessary to facilitate the dehydrogenation and the accompanying hydrogenolysis reactions. As has been shown in a series of works (e.g., refs. [6,7,19–21]), very small ensembles, involving one or two surface platinum atoms can catalyse hydrogenation and dehydrogenation, while the competing hydrogenolysis reactions require pretty large ensembles (catalytic clusters) of size 1 nm and more involving multiple adsorption sites [2,6,7,11,18,20–24]. Correspondingly, the dehydrogenation reaction can be considered structure insensitive, whereas the larger number of contiguous surface atoms of the active phase required for the hydrogenolysis reactions is a prerequisite for their structure sensitivity [6,9,11,21]. Coke formation is also considered to be structure sensitive, as far as coke precursors usually originate from unsaturated surface species tightly bound either to multiple sites on the active phase, or to acidic sites on the support.

Kinetic analysis of processes realized with the participation of different types of active sites is still scarce, due to the necessity to use appropriate models taking into account such an essential peculiarity of these complex reaction systems. The classical model of ideal adsorbed layers has been extended [25] to reactions taking place on two types of sites in close proximity. In ref. [26], an approach is suggested for the kinetic description of processes occurring through a surface collision of species adsorbed on two distinct surface sites of different nature. The model proposed in ref. [27] describes the activity and selectivity of a Pt/SnO_2 catalyst in terms of apolar and polarized types of sites, characterized by different deactivation profiles. Nonetheless, accounting the structure sensitivity of coke formation, it is still of academic and practical interest the development of models focused on the participation of various types of active sites in the course of processes accompanied by catalyst deactivation.

Another aspect of special interest is the contribution of some promoters for increasing the resistance of the Pt catalysts to deactivation by the coke deposits. This phenomenon is of great industrial importance, and detailed knowledge on its mechanism and casual dependencies is both of academic and manufacture interest.

It has been noted in a number of studies (e.g., refs. [7,17,21,28–31]) that smaller size of the Pt ensembles on the surface may result in reduced deactivation. Some authors suggest [21] that steric hindrance for the unsaturated carboneous fragments to meet and form large and highly dehydrogenated species, is of primary importance for the deactivation resistance of catalysts which are characterized by small number of Pt–Pt surface neighbors. These considerations are in line with the concept of the structure sensitivity of coke formation [21,28,29]. The results on isobutane dehydrogenation over silica and L-zeolite-supported Pt catalysts, reported in refs. [7,17,31] are also in support to the suggestion that the formation of carbon depositions may be hindered in the presence of Sn or K because of the provoked effect of reducing the size of the Pt surface ensembles. Similar effects of suppressed coke deposition, along with improved isobutene selectivity, resulting from the addition of optimal amounts of Sn, have been reported in ref. [32].

Table 1
Notations of the partial pressures of the gas-phase species

Species	C_4H_{10}	C_4H_8	C_3H_6	C_2H_4	CH_4	C_2H_6	C_3H_8	H_2
Partial pressure	P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_H

The authors of ref. [15] attach considerable significance as well to the role of adsorbed hydrogen for maintaining the catalyst activity, most probably by impeding coking.

It has been reported in ref. [12] for a Pt–Sn/Al_2O_3 catalyst that, because of the lower strength of adsorption, coke precursors can migrate easily to the support, and this results in reduced coke accumulation over the active sites. The capability of the promoting metal to weaken the adsorption of unsaturated species [33–40] is considered to make for changing the location of coke through spill over the support also by the authors of refs. [18,21,33–35,40].

2. Essence of the experimental data subject to analysis

The model suggested below is based on experimental data presented in a series of studies [41–46] examining the dehydrogenation of isobutane over three γ-Al_2O_3-supported catalysts, namely: 0.35% Pt (further noted as cat_1, 0.90 m^2/g specific surface); 0.35% Pt with 2% In (noted as cat_2, 0.87 m^2/g specific surface); 0.35% Pt with 2% Sn (noted as cat_3, 0.54 m^2/g specific surface). For the sake of lucidity, it would be of use shortly to summarize the experimental observations and some of the essential considerations serving as grounds for the model under concern.

The experiments have been carried out [41–46] in a gradientless flow circulation reactor under the following operating conditions: atmospheric pressure; presence of hydrogen in the feed; space velocity of isobutane within the range 0.42–10 s^{-1}; initial partial pressures of isobutane (P_1) and hydrogen (P_H) in the range from 12.5 to 67 kPa; temperature interval 773–873 K. The notation of partial pressures of the gas-phase components is presented in Table 1. Major accompanying reactions to dehydrogenation were: (i) cracking and (ii) coke formation. Convincing evidence has appeared from the experimental data showing that the addition of Sn or In to the active phase substantially modify the kinetic features of the process.

The rates of dehydrogenation (r) and cracking (r_{cr}) can be described by the following kinetic equations which have been derived in refs. [41,42] on the basis of special kinetic studies.

$$r = \frac{k_1 P_1}{P_2 + k_2\sqrt{P_H}} \quad (1)$$

$$r_{cr} = \frac{k_3 P_1 + k_4 P_2}{P_2 + k_5\sqrt{P_H}} \quad (2)$$

Key experimental data used in the kinetic analysis is presented in Table 2.

It is of importance to note that in case the active phase is pure Pt (cat_1), the values of the coefficients in the denomina-

Table 2
Kinetic data on isobutane dehydrogenation over promoted and unpromoted supported platinum catalysts

T (°C)	Concentration (mmol/l)			Conversion (%)	Reaction rate (mol/(g catalyst h))	
	$[C_4H_{10}]$	$[C_4H_8]$	$[H_2]$		Experimental	Calculated
Catalyst: 0.35% Pt/γ-Al_2O_3 (cat_1)						
500	19	1.3	22	6.5	7.0	7.8
500	19	1.0	21	5.0	8.5	8.6
500	12	1.0	29	7.3	4.7	4.5
540	19	1.2	22	4.0	15.0	14.1
540	18	1.8	22	8.8	11.0	11.0
540	12	1.3	30	10.0	9.9	7.8
570	18	1.8	22	8.9	15.2	18.0
570	11	1.6	31	12.0	10.9	10.0
570	12	1.6	31	11.0	13.9	11.2
600	17	2.5	23	12.0	17.2	21.0
600	18	2.1	22	10.0	25.0	24.0
600	11	1.7	31	13.0	13.2	14.0
Catalyst: (0.35% Pt + 2% In)/γ-Al_2O_3 (cat_2)						
500	9	1.1	23	11.0	36	29
500	19	1.2	23	6.1	60	66
500	17	3.0	13	14.0	66	70
500	19	1.8	12	8.0	110	84
540	4.6	0.4	29	8.3	40	49
540	5.4	0.9	23	12.0	39	52
540	5.8	0.8	23	8.0	55	58
540	8.2	1.5	24	14.0	73	75
540	8.9	1.2	23	12.0	100	87
540	12.0	1.6	23	12.0	130	110
540	18	2.4	23	12.0	130	160
540	18	2.5	15	12.0	180	190
540	18	1.8	11	9.0	200	250
540	18	2.2	8.0	11.0	220	280
540	14	6.5	7.0	31.0	130	140
540	17	3.8	6.0	19.0	200	230
570	6.4	3.5	24	35.0	85	72
570	16.0	4.2	25	21.0	210	210
570	14.0	5.9	16	23.0	210	190
570	15.0	5.6	16	27.0	260	210
600	6.2	3.8	24.0	37.0	130	140
600	12.0	8.0	28.0	39.0	180	170
600	13.0	7.3	18.0	36.0	260	240
Catalyst: (0.35% Pt + 2% Sn)/γ-Al_2O_3 (cat_3)						
500	24.0	3.0	15.0	10.0	151	159
500	17.0	3.0	23.0	13.0	84	85
500	12.0	1.0	30.0	8.0	54	60
540	21.0	6.0	17.0	29.0	312	307
540	15.0	5.0	26.0	26.0	155	168
540	11.0	3.0	33.0	19.0	134	129
570	17.0	11.0	19.0	39.0	285	245
570	12.0	9.0	29.0	42.0	158	138
570	9.0	4.0	36.0	32.0	151	141
600	16.0	11.0	19.0	41.0	448	457
600	10.0	10.0	31.0	50.0	290	237
600	6.0	6.0	40.0	46.0	118	135

tors of the equations for r and r_{cr} are identical, $k_2 = k_5$, which is an indication that the dehydrogenation and cracking steps occur on the same active sites. On the other side, as reported in ref. [44], it can be concluded from the selectivity–conversion curves that on this catalyst the cracking reaction proceeds by a parallel-consecutive route to the dehydrogenation mechanism.

The introduction of In or Sn promoters to Pt has resulted in acceleration of the dehydrogenation rate and in increase of the selectivity. The kinetic equations relevant to the processes occurring on cat_2 and on cat_3 are of similar form as for cat_1, but differ by values of the coefficients. It is essential to accentuate that in the presence of promoters, the coefficients participating in the denominators of the equations describing the dehydrogenation and cracking are of different value, $k_2 \neq k_5$, what points to distinct sites responsible for the realisation of these processes. At the same time, the selectivity–conversion curves exhibited on cat_2 and cat_3 give evidence of parallel proceeding of the dehydrogenation and cracking reactions.

It is of special interest for the present analysis the deactivation peculiarities which have been observed in the course of special experiments carried out [44,46] to examine the influence of coke deposits on the main reaction rate, on the one side, and on the coke formation process, on the other. According to these observations, three stages of the process may be distinguished. During the first, initial stage, the coke formations did not affect the catalyst activity in respect of the main reaction, nor the coke formation rate. The amount of coke deposits increased appreciably with a constant rate until a critical amount c^* of deposited coke was attained. Beyond this threshold the rate of coke formation (r^*) abruptly decreased. It is essential to note the higher values of the threshold amount of c^* in the presence of promoters [44,46]. In the course of the second stage, no apparent change was manifested in regard of the basic reaction rate. Such a quasi-stationary stage with very slowly increasing coke deposits exerted appreciable longitude. Thus, at 813 K, it lasted 7 h for the Pt catalyst, 15 h for Pt with In and 20 h for Pt with Sn promoter. Upon attaining the second threshold value of the coke deposits, further denoted as c^{**}, increase in the coke amount affected the catalyst activity in respect of the main reaction as well. Different values of the second threshold c^{**} have been registered depending on the catalyst composition: according to ref. [44], $c^{**} = 1.8$ wt% for cat_1; 2.3 wt% for cat_2; 6.8 wt% for cat_3. In view of these results, we want to bring the attention to the contribution of In and Sn presence for increasing the catalyst capacity for maintaining stability of action despite the deposited coke.

In this study, the authors make a try to interpret the observed phenomena on the basis of a model assuming the participation of three types of active sites responsible for the behavior of the catalytic system.

3. Assumptions and reaction scheme

As widely recognized in literature, the surface metal atoms inside the active-phase entities may form ensembles of different actual size. Accordingly, the different configurations of these ensembles are responsible for differences in their adsorption ability and mode of action. On the other side, the specificity of the properties and action exerted by the interfacial sites: e.g., Pt/support or Pt/promoter should be not skipped from consideration.

In view of this, it is a proper approximation to postulate the existence of three types of active sites, which we shall further denote as Z-, X- and Y-type. Within the framework of the suggested model, these types of sites can be specified as follows:

Z-type: Single Pt centers, facilitating dehydrogenation. These sites possess strong adsorption affinity for unsaturated hydrocarbons, hydrocarbon fragments and weaker for hydrogen.

X-type: Catalytic clusters (ensembles) involving a number of Pt surface atoms in a proper configuration. These sites are characterised by very strong adsorption affinity. They may involve In or Sn surface atoms, the latter supposed to reduce the adsorption strength of the cluster. The X-type active sites are considered responsible for the C–C bond splitting.

Y-type: Centers on the interfaces Pt/carrier (Y_c) or Pt/promoter (Y_a); $Y = Y_c + Y_a$. The Y-type centers are supposed to facilitate dehydrogenation. Evidences are that these sites are of weaker adsorption strength for hydrocarbons. The adsorption of hydrogen onto them is considered negligible.

The necessity to consider the key elementary steps proceeding on these types of active sites brings to the following reaction scheme:

Adsorption steps	
1. $C_4H_{10} + 2Z \rightarrow HZ + C_4H_9Z$	Slow
2. $C_4H_{10} + Z + X \rightarrow HZ + C_4H_9X$	Slow
3. $C_4H_{10} + Z + Y \rightarrow HZ + C_4H_9Y$	Slow
4. $H_2 + 2Z \leftrightarrow 2HZ$	
Cracking steps	
5. $C_4H_9X + Z \rightarrow CH_3Z + C_3H_6X$	Slow
6. $C_4H_8X + Z \rightarrow CH_3Z + C_3H_5X$	Slow
7. $C_4H_8X + Z \rightarrow C_2H_4X + C_2H_4Z$	Slow
8. $C_4H_9X + Z \rightarrow C_2H_4X + C_2H_5Z$	Slow
9. $C_3H_5X + HZ \rightarrow CH_3Z + C_2H_3X$	
10. $C_2H_3X + HZ \leftrightarrow Z + C_2H_4X$	
Dehydrogenation and desorption steps	
11. $C_4H_9Z + Z \leftrightarrow HZ + C_4H_8Z$	
12. $C_4H_9X + Z \leftrightarrow HZ + C_4H_8X$	
13. $C_4H_9Y + Z \leftrightarrow HZ + C_4H_8Y$	
14. $C_4H_8Z \leftrightarrow Z + C_4H_8$	Slow
15. $C_4H_8Y \leftrightarrow Y + C_4H_8$	
16. $C_2H_5Z + Z \leftrightarrow HZ + C_2H_4Z$	
17. $C_2H_4Z \leftrightarrow C_2H_4 + Z$	Slow
18. $C_3H_5X + HZ \leftrightarrow C_3H_6X + Z$	
19. $C_3H_6X \leftrightarrow C_3H_6 + X$	Slow
20. $C_2H_4X \leftrightarrow C_2H_4 + X$	Slow
21. $C_2H_4Y \leftrightarrow C_2H_4 + Y$	
22. $C_2H_5Z + HZ \leftrightarrow C_2H_6 + 2Z$	
23. $CH_3Z + HZ \leftrightarrow CH_4 + 2Z$	
Migration steps	
24. $C_2H_4Z + Y \leftrightarrow C_2H_4Y + Z$	
25.$C_2H_4X + Y \leftrightarrow C_2H_4Y + X$	
26. $C_2H_4X + Z \leftrightarrow C_2H_4Z + X$	
27. $C_3H_6X + Y \leftrightarrow C_3H_6Y + X$	
28. $C_4H_8X + Y \leftrightarrow C_4H_8Y + X$	
29. $C_4H_8Z + Y \leftrightarrow C_4H_8Y + Z$	
Formation of coke precursors	
30. $C_4H_8X + C_4H_8 \rightarrow C_8H_{16}X$	($\equiv C_nH_mX$; $m \leq 2n$)
31. $C_3H_5X + C_4H_8 \rightarrow C_7H_{13}X$	($\equiv C_nH_mX$; $m \leq 2n$)
32. $C_2H_3X + C_4H_8 \rightarrow C_6H_{11}X$	($\equiv C_nH_mX$; $m \leq 2n$)
33. $C_nH_mX + Z \rightarrow$ Prec1 (on internal sites)	Limiting for coke formation
34. Prec1 + Y → Prec2 + X	Fast
35. $C_nH_mY \rightarrow$ Prec2 (on interface sites)	Limiting for coke formation
Terminating the route of formation of coke precursors	
36. $C_nH_mX + HZ \leftrightarrow$ saturation	Fast

According to experimental data obtained earlier [42], the limiting step for dehydrogenation is the removal of the first hydrogen atom via dissociative adsorption into HZ and half-

Table 3
Notations of the surface concentrations of the different types of active sites and the related intermediates

Intermediates related to the Z-type active sites		Intermediates related to the X-type active sites		Intermediates related to the Y-type active sites	
Surface fraction	Intermediate	Surface fraction	Intermediate	Surface fraction	Intermediate
θ	Unoccupied Z-type sites	ψ	Unoccupied X-type sites	λ	Unoccupied Y-type sites
θ_1	C_4H_9Z	ψ_1	C_4H_9X	λ_1	C_4H_9Y
θ_2	C_4H_8Z	ψ_2	C_4H_8X	λ_2	C_4H_8Y
θ_3	C_4H_5Z	ψ_3	C_3H_6X	λ_3	C_3H_6Y
θ_4	C_4H_4Z	ψ_4	C_2H_4X	λ_4	C_2H_4Y
θ_5	CH_3Z	ψ_5	C_3H_5X	λ_5	C_3H_5Y
θ_H	HZ	ψ_6	C_2H_3X	λ_6	C_2H_3Y
μ_1	Coke precursors Prec1-type	μ_1	Coke precursors Prec1-type	μ_2	Coke precursors Prec2-type

hydrogenated intermediates, which undergo quick transformations. Regarding the reaction scheme suggested above, steps 1 and 3 control the rate of dehydrogenation.

The limiting steps for cracking – rupture of the C–C bonds – are supposed to proceed on X-type sites which are ensembles of surface metal atoms inside the Pt islands. The slow steps are marked as steps 5–8 of the reaction scheme, step 7 considered responsible for olefin cracking and step 8 responsible for the paraffin cracking. Because of the pronounced adsorption strength of the X-type sites, the intermediates formed onto them have longer residence time than the other intermediates. This is a substantial requisite that some of these intermediates give rise to creation of coke precursors (noted as Prec1 in the reaction scheme). Such an assumption is in accordance with data published in literature (e.g., ref. [23]), evidencing that similar Pt ensembles are involved in hydrogenolysis and coke formation reactions.

Two types of coke precursors (further noted as Prec1 and Prec2) are suggested to be of significance for the coke formation. Prec1 are the precursors arising inside the active-phase islands, predominantly on X-type sites. It should be taken into account that the proximity of adsorbed hydrogen forms creates conditions for surface collisions resulting in breaking the chain of coke generation from these precursors. The precursors located onto Y-type sites are noted as Prec2. Their origin is to a considerable extent conditioned by the migration of Prec1 from the interior of the active-phase entities (as considered by step 34 of the reaction scheme). As far as the adsorption of hydrogen on the interfacial sites is negligible, the evolution of the Prec2 precursors into coke with possible spill over the support is not impeded by surface interactions terminating the coking chain. It has been shown by Kogan et al. [3,35], on detailed studies of the catalysts under concern by use of IR-spectroscopy (CO adsorption), DTA, EPR, XPS and other methods, that the migration of coke precursors formed in the interior of the metal-phase islands towards the interfaces with the support is facilitated in the presence of In or Sn promoters. IR-spectroscopy evidence is presented about the contribution of these promoters for weakening the strength of the centers of tight adsorption. Similar evidences have been also reported in studies by other authors (e.g., refs. [21,22,32,35,38–40]).

The coke generated on the support is also of special concern. As well-documented in the literature, acidic sites on the alumina support can lead to the formation of coke deposits. For the sake of completeness, coke precursors created on these sites may be specified as a distinct type (Prec3). It is a widely recognized assumption that the generation of coke precursors is limiting for the coke formation process. Since the content of promoters is of the range of 2%, it is reasonable to suppose that their influence on the performance of the support sites can be neglected. Therefore, we can assume that the rate of generation of Prec3, and correspondingly, the rate of independent coke formation on the support, is not influenced by the presence of promoters. Concerning the increase of coke accumulated on the support at the expense of promoter-enhanced migration of precursors from the active phase, the rate of formation of this portion of support-located coke should be related to the rate of formation of Prec1 and Prec2 precursors. Another point of concern is the deactivation pattern caused by the coke located on the support. Special tests performed in refs. [44,46] gave evidence that the basic dehydrogenation reaction does not proceed on those alumina sites which are not interfacial with the active phase. In view of this, it can be considered that the coke located on the support does not affect the catalytic performance for the cases of kinetic control on the process. Regarding the reaction systems under investigation, the tests have been performed under conditions entirely eliminating the diffusion constraints. Altogether, these considerations give grounds to suggest a model correlating the deactivation pattern with the creation and evolution of the Prec1 and Prec2 coke precursors, and neglecting the effect of promoters on the formation rate and action of coke on the support.

In the present analysis, we would like as well to distinguish the behavior of coke precursors Prec1 located inside the Pt domains from the behavior of coke precursors Prec2 located on the interfacial (Y-type) active sites.

4. Discussion

In this section, the authors make a try to explain some of the mentioned observed effects resulting from the addition of Sn or In to the Pt/γ-Al_2O_3 catalyst from the viewpoint of the suggested postulates and reaction scheme.

We shall denote by ψ the surface concentration of X-type active sites; by θ the surface concentration of Z-type active sites; by λ_c and λ_a the surface concentrations of Y_c- and Y_a-type active sites, correspondingly. All the notations concerning the surface concentrations of the adsorbed intermediates are listed in Table 3.

As stated above, the main dehydrogenation reaction is assumed to proceed on single active sites which are specified either as Z-type sites (located inside the Pt islands), or as Y-type sites (located on the interfaces Pt/carrier (Y_c) or Pt/promoter (Y_a); $Y = Y_c + Y_a$). Considering that the rates of steps (1) and (3) of the suggested reaction scheme are limiting for dehydrogenation, the kinetic equation derived on the basis of the law of acting surfaces takes the form:

$$r_{dh} = \frac{k_6 P_1}{\alpha(P_2 + P_3 + P_4) + \alpha_H \sqrt{P_H}} [C_1 \lambda + \theta] \quad (3)$$

where C_1 is a coefficient associated with the ratio of the rates of steps 1 and 3 of the scheme, α the adsorption coefficients of the olefin products and α_H is the adsorption coefficient of hydrogen.

Considering that the concentration of isobutene significantly exceeds the concentrations of the lower olefins, $P_2 \gg > P_3 + P_4$, Eq. (3) is transformed into:

$$r_{dh} = \frac{k_6 P_1}{\alpha P_2 + \alpha_H \sqrt{P_H}} [C_1 \lambda + \theta] \quad (4)$$

If we incorporate the term in the brackets into the rate coefficient constant, Eq. (4) coincides in form with the experimentally established Eq. (1) describing the dehydrogenation rate. The term in the brackets allows for distinguishing the contribution of Z-sites (θ) from the contribution of Y-sites (λ). If the contribution of the Z-sites is of major importance, the value of θ appreciably exceeding the value of $(C_1\lambda)$, the contribution of Y-sites may be disguised. This may be the case when the catalyst is Pt/Al_2O_3, since for this catalyst $Y_a = 0$ and $Y = Y_c$. A part of the Pt atoms inside the Pt islands are engaged in X-sites that make for cracking of either isobutane or isobutene. As far as surface Pt atoms inside the entities are at the same time engaged in Z-type active sites catalysing the dehydrogenation, the similarity of the coefficients in the denominators of the kinetic equations for dehydrogenation and cracking over cat_1 can be interpreted as reflecting the fact that both reactions are realized predominantly over the active metal phase inside the Pt islands.

The introduction of promoters reduces the adsorption affinity of all types of sites. As a result, the activation energy values decrease, and this leads to higher reaction rates of both dehydrogenation and cracking (as observed experimentally).

In the presence of promoters, $Y = Y_c + Y_a$. Therefore, the number of Y-type sites responsible for dehydrogenation would increase. Possible change of the apparent kinetics may be caused by the fact that the equilibrium between Z- and Y-sites changes in favor of the fraction of Y-centers. Obviously, the contribution of Y to the catalytic action becomes essential when their fraction exceeds a certain threshold value. In addition, compared to Z-type sites, Y_a-sites are supposed to be of weaker adsorption strength. Easier desorption of olefins formed on them is supposed to reduce the fraction of these sites which are out of action being blocked by adsorbed olefins. The increased number of interfacial active sites, in combination with the provoked increase of their activity, is to bring the system to a point that the contribution of Y-type sites to dehydrogenation will be comparable, or even exceed the contribution of Z-sites. Considering that cracking occurs onto Pt atoms engaged in X-sites inside the Pt islands, the apparent manifestation of the phenomenon may be interpreted as proceeding of dehydrogenation and cracking in parallel on independent sites. Following this model, one can explain the experimentally observed conversion–selectivity curves relevant to the process in the presence of In or Sn, namely: the selectivity increases and becomes independent of conversion, what is characteristic of parallel proceeding.

The behavior of the catalytic system connected with two threshold concentrations of coke formations, and the influence of the promoter on the threshold amounts of coke disturbing the stationary proceeding are of special interest.

The experimental studies carried out in refs. [44,46] have presented evidence about the contribution of isobutene to coke formation. In accord with the suggested reaction scheme, we postulate that coke precursors are likely to arise because of interactions of isobutene with unsaturated surface intermediates located predominantly on X-type sites (steps 30–33 of the scheme). $C_8H_{16}X$, $C_7H_{13}X$ and $C_6H_{11}X$ (denoted as C_nH_mX, for $m \le 2n$) species are supposed either to give rise to coke precursors of Prec1 type, involving neighboring Pt atoms, or to migrate to the interface sites, where C_nH_mY species gives rise to coke precursors of Prec2 type. It is essential to note that the proximity of the intermediates of adsorbed hydrogen [HZ], creates conditions for surface collisions resulting in breaking the chain of coke formation from these precursors. At the same time, the Prec2 precursors are not supposed to undergo surface collisions with adsorbed hydrogen, as far as hydrogen does not adsorb on the interfacial sites. This seems to be the most probable reason for the apparent observation that the Prec2 precursors evolve into coke more readily than the precursors inside the Pt domains.

If we denote by r_P^* the rate of coke formation inside the Pt entities, and by r_Y^* the rate of coke formation originating from Prec2 precursors, the rate of coke formation on the active phase (r^*) can be presented as:

$$r^* = r_P^* + r_Y^* \quad (5)$$

In accord with the reaction scheme,

$$r_P^* = k^* \mu_1 - k_{36} \mu_1 \theta_H \quad (6)$$

$$r_Y^* = k^* \mu_2 \quad (7)$$

where μ_1 and μ_2 are the surface concentrations of Prec1 and Prec2 coke precursors, correspondingly.

Since the migration of the precursors is fast, it can be assumed that Prec1 and Prec2 are in equilibrium, following the relation:

$$\mu_2 = \mu_1 K_m \left(\frac{\lambda}{\psi} \right) \quad (8)$$

λ denotes the fraction of unoccupied interfacial (Y-type) sites and ψ denotes the surface concentration of unoccupied X-type sites (catalytic clusters). Under quasi-stationary conditions, while the main and cracking reactions do not “feel” the influence of coke, it can be assumed that λ, ψ and θ_H keep quasi-constant values. Substituting $K_s = k_{36}/k^*$, and Eq. (8) for μ_2, the coke formation rate may be presented as:

$$r^* = r_P^* + r_Y^* = \mu_1 \left[k^* \left(1 + K_m \left(\frac{\lambda}{\psi} \right) - K_s \theta_H \right) \right] \tag{9}$$

It can be assumed about the variation of r^* in time

$$\frac{\partial r^*}{\partial t} = \frac{\partial \mu_1}{\partial t} k^* \left[1 + K_m \left(\frac{\lambda}{\psi} \right) - K_s \theta_H \right] \tag{10}$$

The coefficient K_s formally considers the impact of terminating the chain of coke formation (step 36 of the reaction scheme).

Regarding the first stage of the process, during which the coke formation rate r^* is practically constant, it can be assumed

$$\frac{\partial r^*}{\partial t} \approx 0 \tag{11}$$

Since the amount of coke increases in the course of this stage, $(\partial \mu_1 / \partial t) > 0$, and it follows from Eqs. (10) and (11) that

$$1 + K_m \left(\frac{\lambda}{\psi} \right) - K_s \theta_H \approx 0 \tag{12}$$

Eq. (12) can be transformed into

$$\lambda \approx \frac{\psi [K_s \theta_H - 1]}{K_m} \tag{13}$$

The surface concentrations of λ, ψ and θ_H are in fact quasi-stationary, being to a certain extent affected by the coverage of coke or coke precursors. While these changes compensate each other so that the condition (13) can be kept, the rate of coke formation keeps constant. Evidently, the Y-type sites are stronger affected in the course of coke formation, as the Prec2 coke precursors do not participate in reaction steps breaking the chain of coke formation. Therefore, it can be assumed that the reaction system will come to a point for which the condition (13) is changed into

$$\lambda < \frac{\psi [K_s \theta_H - 1]}{K_m} \tag{14}$$

Condition (14) is equivalent to the condition of decreasing rate of coke formation:

$$\left(\frac{\partial r^*}{\partial t} \right) < 0 \tag{15}$$

It should be noted that $\lambda = \lambda_c$ in case the process is carried out over cat_1 and $\lambda = \lambda_c + \lambda_a$ for the cases of cat_2 and cat_3 which contain In or Sn as promoters. Naturally, $\lambda_c + \lambda_a > \lambda_c$, or in the presence of promoters, the "capacity" of Y-type sites for keeping the quasi-stationary condition (13) would be higher. A logic explanation of the experimental observation [45,46] is that the introduction of the promoters results in higher values (c^*) of the threshold amount of coke needed to bring the catalytic system to the second phase.

Eqs. (3) and (4) may be helpful in interpreting the fact that the dehydrogenation rate is affected upon attaining higher threshold values of coke depositions in the presence of promoters. The Y-type sites seem to be very active, and for this reason their decrease in number exerts not an apparent influence on the common catalyst activity before reaching a threshold limit c^{**}. This threshold value should be related to the surface concentration of Y-sites. The latter noticeably increases in the presence of promoters: $\lambda = \lambda_c + \lambda_a$ against $\lambda = \lambda_c$ for the unpromoted catalyst. In addition, the capability of promoters to enhance the migration of the Prec1 coke precursors to the interfacial Y_c- and Y_a-sites is allowing the spill of coke precursors over the support, where coke would not deteriorate the catalyst activity in regard of dehydrogenation. This is one of the probable reasons that in the presence of promoters the threshold amount of coke c^{**} governing the coke tolerance effect markedly increased.

5. Conclusions

The analysis of the experimental data obtained earlier brought the authors to the necessity to suggest a model considering the participation of three types of active sites in the course of isobutane dehydrogenation over the investigated promoted and unpromoted alumina-supported platinum catalysts. It has been recognized in numerous literature studies that: (i) active sites consisting of single Pt atoms have catalytic action different from the sites involving ensembles in proper configuration and (ii) the properties of the active sites inside the active-phase entities differ from the properties of the sites on the interfaces Pt/support or Pt/promoter. Describing such systems by means of a common Langmuir–Hinshelwood equation is an approximation used to avoid the mathematical complexity, and such an approach is applicable in a number of cases when the impact of surface ununiformity can be neglected. However, when the surface ununiformity effects are not negligible, a different approach for the kinetic description is necessary. By this study, the authors are aiming to make a contribution to developing models taking into account the diversity in the properties of different active sites. To explain the observed peculiarities of the catalytic system under investigation, the model distinguishes the contribution of the following three types of active sites: single Pt centers of strong adsorption affinity facilitating dehydrogenation; catalytic clusters involving a number of Pt (and possibly Sn or In) surface atoms in proper configuration facilitating cracking; and centers on the interfaces Pt/carrier or Pt/promoter of weaker adsorption ability. Two types of precursors responsible for the coke formation are postulated: precursors arising from intermediates tightly adsorbed onto the catalytic clusters inside the active-phase islands; and precursors located onto the interfacial sites in consequence of the migration of the first type of precursors. A detailed reaction scheme is proposed considering the impact of coke located on different types of sites for the evolution of the reaction system. The relations following from the suggested model qualitatively explain the experimentally observed stepwise character of the deactivation kinetics, as well as other promoter-provoked effects.

The suggested explanations will be subject of additional verification and proof. Further light onto the problem would call forth better understanding of the intimate reaction mechanism, what is of primary importance for the optimal process design.

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