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Kinetics of Benzene and Toluene Hydrogenation on a Pt/TiO_2 Catalyst

R. V. Kazantsev*, N. A. Gaidai*, N. V. Nekrasov*, K. Tenchev, L. Petrov**, and A. L. Lapidus***

** Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia*

*** Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, Bulgaria*

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Abstract—The kinetics and mechanism of benzene and toluene hydrogenation on a Pt/TiO_2 catalyst were studied in steady-state and non-steady-state regimes in the presence or absence of strong metal–support interactions (SMSI). It was found that the kinetics and mechanism of the test reactions were independent of SMSI. The observed effect of a decrease in the catalytic activity in the SMSI state was due to structural changes in the active centers of the catalyst and to the presence of strongly bound hydrogen species on the surface; this was also supported by thermal-desorption data.

INTRODUCTION

The strong metal–support interaction (SMSI) became the subject matter of many works after the publication of the study by Tauster *et al.* [1], who proposed this term to designate interactions observed after the reduction of metals supported on reducible transition element oxides at moderately high temperatures. Since the mid-1980s, the problem of SMSI has attracted considerable interest, as evidenced by a number of review articles [2–5]. However, the majority of publications were devoted to studies of this phenomenon with the use of physicochemical techniques, whereas its kinetic aspect has remained almost unstudied. Only a few publications contained the results of kinetic studies performed on catalysts in the presence of SMSI [6–10].

TiO_2 is the most typical and best studied support for the demonstration of the SMSI effect. The majority of studies of this effect on TiO_2 were performed with the use of Degussa P25 powder, which contained 85% anatase and 15% rutile [11].

In this work, we studied the reaction kinetics of benzene and toluene hydrogenation in steady-state and non-steady-state regimes in the presence or absence of SMSI. Moreover, temperature-programmed desorption (TPD) of hydrogen was used to study this effect.

EXPERIMENTAL

Kinetic experiments in a steady-state region were performed in a flow-circulation system at atmospheric pressure with the dilution of the reaction mixture with helium. The reaction mixture was analyzed on an LKhM-8MD chromatograph.

Transient kinetic studies were performed in a special low-volume unit by the response technique [12] with the use of an MSKh-6 time-of-flight mass spectrometer as the detecting instrument.

The composition of the reaction mixture at the reactor outlet was analyzed at 1-s intervals. The concentrations of benzene and cyclohexane were evaluated from molecular peaks (mass numbers of 78 and 84, respectively). Changes in the concentrations of toluene and methylcyclohexane were monitored using fragment peaks with mass numbers of 91 and 83, respectively (the greatest peaks in the mass spectra of the above compounds).

The residence time, that is, the ratio of the volume of the reaction mixture to the flow rate, was no longer than 7 s; the measurements were performed after this time. In all the experiments, the relaxation time was shorter than the reaction turnover time (the number of active centers was taken as equal to 10^{19} m^{-2}); this can be considered as an argument for classifying the relaxations tested as intrinsic relaxations.

To write response conditions, we used a notation system in which a slash corresponded to a stepwise change in the composition of the mixture supplied to the reactor. The resulting relaxation curves characterized changes in the concentration of a substance because of the last change in the composition of the mixture. The interpretation of results was based on a set of all the relaxation curves obtained.

Platinum catalysts on titanium dioxide powders (ultradispersed rutile[1] and Degussa P25) were used in this study. The 3% Pt/TiO_2 (rutile), 1% Pt/TiO_2 (Degussa P25), and 1% Pt/SiO_2 catalysts were prepared by impregnating the supports with an aqueous solution of H_2PtCl_6. Before the impregnation, the support was calcined in an oxygen atmosphere (P = 0.27 atm) at 530°C for 3 h. After the impregnation, the sample was

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[1] The ultradispersed rutile was synthesized by Yu.M. Shul'ga at the Institute of Problems of Chemical Physics, Russian Academy of Sciences.

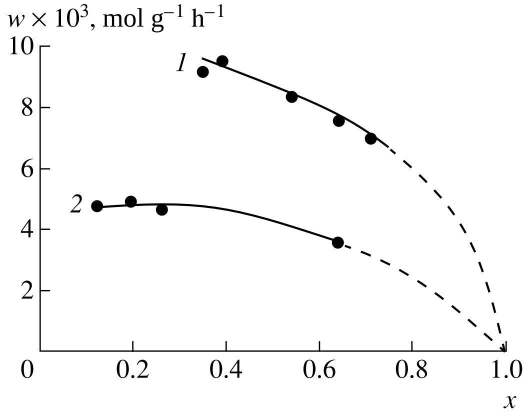

Fig. 1. Dependence of the rates of (*1*) benzene and (*2*) toluene hydrogenation on conversion at 160°C after the reduction of a Pt/TiO_2 (rutile) catalyst at 200°C.

dried in air with continuous stirring initially at 80–90°C for 3–6 h and then at 120–130°C for 1 h. The specific surface areas of the supports were as follows (m^2/g):

TiO_2(rutile),	95
TiO_2(Degussa P25),	40
SiO_2,	180

The dispersity of the catalysts based on rutile was 0.35, as measured by the solubility method [13]. The dispersity of the catalyst based on TiO_2 (Degussa P25), which was measured by Shpiro *et al.* [14], was equal to 0.65. The dispersity of the catalysts remained unchanged under the conditions of our experiments; consequently, the observed effect cannot be due to agglomeration processes. For comparison, we studied the reaction kinetics of benzene hydrogenation on a Pt/SiO_2 catalyst, the reduction temperature of which had no effect on its activity [2]. The portions (1 g or smaller) of catalysts with a particle size of 0.5–1.0 mm were loaded into the reactor.

The thermal-desorption measurements were performed using a setup based on a differential scanning calorimeter. A chromatograph was used as the detecting instrument. The temperature of hydrogen adsorption was chosen in accordance with the temperature range in which the kinetic studies were performed. The TPD of hydrogen was performed over the temperature range 130–600°C at a rate of 15°C/min. Catalyst portions (0.1–0.2 g) were loaded into the reactor.

RESULTS AND DISCUSSION

The kinetics of benzene hydrogenation was studied on Pt/SiO_2 (reduced at 300 and 500°C) and Pt/TiO_2 (Degussa P25) (reduced at 200 and 500°C) catalysts over a temperature range of 130–180°C at initial partial pressures of benzene and hydrogen of 0.071–0.183 and 0.35–0.93 atm, respectively. The conversion varied from 0.03 to 0.92.

The kinetics of toluene hydrogenation was studied on a Pt/TiO_2 (rutile) catalyst reduced at 200, 300, 400, and 500°C. The reaction temperature was 130–180°C; the initial partial pressures of toluene and hydrogen were 0.027–0.055 and 0.30–0.97 atm, respectively. The conversion varied from 0.04 to 0.64.

Under these conditions, the reactions of benzene and toluene hydrogenation occurred selectively, and the only products were cyclohexane and methylcyclohexane, respectively.

At a constant space velocity and unchanged initial concentrations of benzene (toluene) and hydrogen, the reaction rate was independent of the linear velocity of a circulating flow; consequently, external diffusion had no inhibiting effect. A comparison between the rates of benzene and toluene hydrogenation, which was performed on varying catalyst particle size at 180°C, demonstrated that internal-diffusion inhibition was absent from catalyst granules with a size of no greater than 1 mm. Hence it follows that the reactions occurred in the kinetic region.

Figure 1 demonstrates the conversion curves (the conversion dependence of the reaction rate) [15]. The introduction of cyclohexane or methylcyclohexane into the initial mixture in amounts much greater than those formed in the course of hydrogenation did not affect the reaction rates over the entire range of test temperatures; consequently, inhibition by the reaction products was absent.

The curves of the temperature dependence of the test reaction rates cannot be linearized in Arrhenius coordinates over a range of 130–180°C. Therefore, the dependence of the reaction rates on the partial pressures of components cannot be expressed by an exponential equation. To describe the data obtained, we used the following equation, which was derived previously for benzene and toluene hydrogenation on a platinum–alumina catalyst under analogous conditions [16] with consideration for catalyst surface heterogeneity [17]:

$$w = \frac{kP_{H_2}^n P_b \gamma}{(P_{H_2}^{0.5} + k_1 P_{H_2} + k_2 P_b + k_i \Sigma P_b P_{H_2}^m)^{2\alpha}},$$

where α is a coefficient of linear relationship, $0 \le \alpha \le 1$ (the values $\alpha = 0$ and 1 formally correspond to the occurrence of the reaction in the regions of low and high catalyst surface coverages, respectively); k, k_1, k_2, and k_i are constants; γ is a coefficient that takes into account the influence of a reverse reaction; n and m are exponents. The terms $P_{H_2}^{0.5}$ and $k_2 P_{H_2}$ correspond to surface coverages with atomic or dissociatively adsorbed and molecular hydrogen, respectively. The last term in the denominator characterizes surface coverage with various incompletely hydrogenated species. The contribution of these terms was insignificant, and

Table 1. Kinetic data on benzene hydrogenation on Pt/SiO_2 and Pt/TiO_2 (Degussa P25) catalysts

Conversion	P_b, atm	P_{H_2}, atm	$w_{expt} \times 10^2$, mol g^{-1} h^{-1}	$w_{calcd} \times 10^2$, mol g^{-1} h^{-1}
Pt/SiO_2				
0.61	0.044	0.31	1.24	1.15
0.33	0.075	0.31	1.53	1.47
0.18	0.086	0.31	1.60	1.55
0.40	0.060	0.54	1.89	1.89
0.34	0.071	0.54	2.23	2.05
0.24	0.086	0.53	2.43	2.24
0.50	0.060	0.88	2.37	2.45
0.35	0.089	0.86	3.23	3.06
0.22	0.102	0.87	3.64	3.30
Pt/TiO_2 (Degussa P25) T_{red} = 200°C				
0.44	0.085	0.30	1.21	1.40
0.22	0.097	0.31	1.57	1.38
0.58	0.054	0.52	4.54	3.94
0.39	0.086	0.52	4.06	3.40
0.71	0.039	0.87	7.65	7.33
0.54	0.062	0.87	8.12	7.58
0.39	0.078	0.87	8.54	7.49
Pt/TiO_2 (Degussa P25) T_{red} = 500°C				
0.22	0.098	0.31	0.58	0.57
0.10	0.109	0.31	0.64	0.58
0.31	0.088	0.52	1.12	1.09
0.10	0.103	0.53	1.38	1.16
0.22	0.086	0.89	2.14	1.93
0.15	0.097	0.89	2.23	2.03

Table 2. Kinetic data on toluene hydrogenation on a Pt/TiO_2 (rutile) catalyst

Conversion	P_t, atm	P_{H_2}, atm	$w_{expt} \times 10^3$, mol g^{-1} h^{-1}	$w_{calcd} \times 10^3$, mol g^{-1} h^{-1}
T_{red} = 200°C				
0.18	0.040	0.29	0.49	0.49
0.06	0.045	0.29	0.52	0.45
0.23	0.037	0.48	1.25	1.22
0.07	0.045	0.48	1.18	1.10
0.20	0.038	0.67	2.39	2.08
0.12	0.043	0.67	2.27	1.96
0.64	0.013	0.96	3.63	3.76
0.36	0.031	0.95	4.24	3.76
T_{red} = 300°C				
0.13	0.029	0.29	0.31	0.33
0.06	0.032	0.29	0.36	0.33
0.20	0.028	0.48	0.67	0.66
0.08	0.032	0.48	0.69	0.67
0.32	0.024	0.68	1.01	0.97
0.20	0.028	0.68	1.12	1.01
0.19	0.028	0.97	1.64	1.53
0.10	0.031	0.97	1.68	1.58
T_{red} = 400°C				
0.06	0.030	0.29	0.08	0.07
0.09	0.028	0.48	0.15	0.15
0.09	0.045	0.67	0.25	0.23
0.11	0.045	0.95	0.42	0.40
T_{red} = 500°C, calcination in helium at 600°C				
0.08	0.035	0.29	0.31	0.33
0.08	0.042	0.48	0.69	0.67
0.10	0.041	0.67	1.19	1.16
0.12	0.048	0.95	1.97	1.84

they could be ignored. Nine equations were obtained taking the addition of the first ($n = 1$), second ($n = 2$), or third ($n = 3$) hydrogen molecule to the benzene ring as a rate-limiting step and varying the coefficient α of linear relationship (0, 0.5, and 1). The discrimination of the equations was performed using the following criteria: (1) the mean-square deviations should be no greater than the determination error of the reaction rate, which was estimated at 8%, and (2) the shapes of calculated curves should be consistent with experimental points.

Tables 1 and 2 summarize kinetic data on the hydrogenation of benzene and toluene.

We found by calculations that the following equation provided the best fit to the experimental data obtained on the Pt/SiO_2 catalyst:

$$w = \frac{kP_{H_2}P_b}{P_{H_2}^{0.5} + k_1P_{H_2} + k_2P_b}, \tag{1}$$

where $k = 1.77$ mol g^{-1} h^{-1} $atm^{-1.5}$, $k_1 = 1.7$ $atm^{-0.5}$, and $k_2 = 23$ $atm^{-0.5}$.

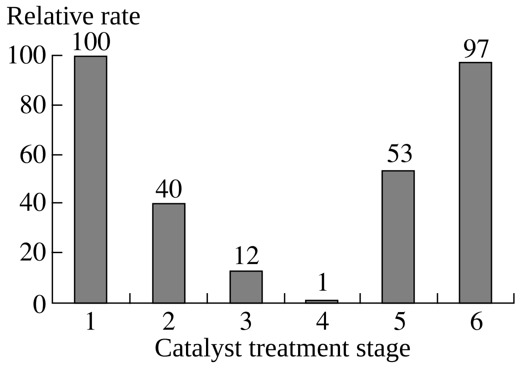

Fig. 2. Relative rate of toluene hydrogenation on a Pt/TiO_2 catalyst depending on the successive treatment of the catalyst. Treatment stages: (*1–4*) reduction at 200, 300, 400, and 500°C, respectively; (*5*) calcination in helium (600°C); and (*6*) oxidation with air with subsequent reduction (200°C).

At a reaction temperature of 160°C, the following equation was best suited to describe the experimental data obtained after the reduction of the Pt/TiO_2 (Degussa P25) catalyst at 200°C:

$$w = \frac{k' P_{H_2}^2 P_b}{(P_{H_2}^{0.5} + k_1 P_{H_2} + k_2 P_b)^2}. \qquad (2)$$

The same equation describes data obtained on this catalyst after reduction at 500°C, with the only difference that the values of constants are smaller in the latter case (Table 3).

The following equation provided the best fit to the experimental data obtained in the reaction of toluene hydrogenation on the Pt/TiO_2 catalyst over a temperature range of 130–160°C:

$$w = \frac{k' P_{H_2}^2 P_t}{(P_{H_2}^{0.5} + k_1 P_{H_2} + k_2 P_t)^2}. \qquad (3)$$

The constants of this equation decreased as the catalyst reduction temperature was increased (Table 4).

The form of rate equations remained unchanged as the catalyst reduction temperature was varied; this fact suggests that SMSI had no effect on the kinetics of the test reactions.

The exponent at the partial pressure of hydrogen in the numerator, which is equal to 1 or 2 in the case of Pt/SiO_2 or Pt/TiO_2 catalysts, respectively, indicates that the addition of the first or second hydrogen molecule to the benzene ring can be a rate-limiting step in the former or latter case, respectively.

The overall exponent of the denominator, which is equal to 1 or 2 for Pt/SiO_2 or Pt/TiO_2 catalysts, respectively, may be indicative of the occurrence of these reactions at different surface coverage regions of these catalysts [17]. In the case of benzene on Pt/SiO_2, the reaction occurs in the region of medium coverages, whereas on Pt/TiO_2 catalysts it occurs in the region of high coverages for benzene and toluene.

Figure 2 demonstrates the relative reaction rates of toluene hydrogenation on Pt/TiO_2 (rutile), where the reaction rate after reduction at 200°C was taken as 100%, with different catalyst treatment procedures performed in sequence. The catalyst activity, which decreased as the temperature of reduction with hydrogen was increased, increased by one-half of the initial value after purging with helium for 2 h at 600°C, whereas it almost reached the initial level after oxidation at 200°C followed by reduction at this temperature.

Consequently, the overall SMSI effect observed can be subdivided into two components: (1) a decrease in the catalytic activity due to structural changes in active centers on the catalyst surface and (2) a decrease in the catalytic activity due to the presence of strongly bound hydrogen species adsorbed on the catalyst.

One of the main problems in studies of the mechanism of a heterogeneous catalytic reaction is the interaction between components; that is, whether they enter into the reaction from an adsorbed state or directly from a gas phase. The shape of a rate equation cannot clearly indicate the character of interactions between reactants and transformations of reaction intermediates.

To obtain information on the reaction mechanism and to refine the form of the rate equation, we studied transient processes of attaining a steady state in the reactions of benzene and toluene hydrogenation by the response technique. This technique consists in the detection of changes in the concentrations of reactants or reaction products at the reactor outlet upon an abrupt change in the composition of the reaction mixture.

Table 3. Constants in Eq. (2) at 160°C

T_{red}, °C	k', mol g^{-1} h^{-1} atm^{-2}	k_1, $atm^{-0.5}$	k_2, $atm^{-0.5}$
200	28.4	1.23	35.1
500	1.00	0.49	5.78

Table 4. Constants in Eq. (3) at 160°C

T_{red}, °C	k', mol g^{-1} h^{-1} atm^{-2}	k_1, $atm^{-0.5}$	k_2, $atm^{-0.5}$
200	2.95	0.95	90.8
300	0.32	0.57	28.7
400	0.05	0.16	25.3
500*	0.49	0.75	47.3

* With subsequent calcination in a helium flow at 600°C.

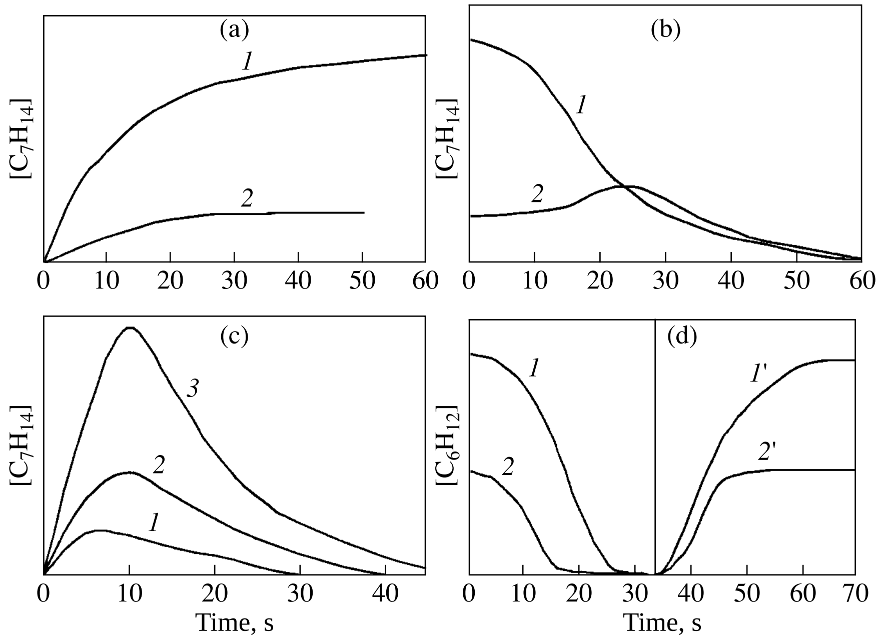

Fig. 3. Methylcyclohexane and cyclohexane concentration changes in the responses: (a) $H_2/(H_2 + C_7H_8)$ at 176°C after catalyst reduction at (*1*) 200 and (*2*) 400°C; (b) (*1*) $(H_2 + C_7H_8)/H_2$ and (*2*) $(H_2 + He + C_7H_8)/(H_2 + He)$ at 140°C after catalyst reduction at 200°C; (c) (*1, 2*) $(He + C_7H_8)/He/H_2$ and (*3*) $(He + C_7H_8)/H_2$ at 140°C after catalyst reduction at 200°C. The duration of purging with helium was (*1*) 3 or (*2*) 1 min; (d) (*1, 2*) $(H_2 + C_6H_6)/H_2$ and (*1*', *2*') $H_2/(H_2 + C_6H_6)$ at 180°C after catalyst reduction at (*1, 1*') 200 or (*2, 2*') 400°C.

The experiments were performed over the temperature range 110–190°C with the Pt/TiO_2 (rutile) catalyst reduced at 200 and 400°C. The initial partial pressures of benzene, toluene, and hydrogen were varied within the ranges 0.080–0.120, 0.020–0.040, and 0.5–1.0 atm, respectively. Figure 3a demonstrates relaxation curves, which illustrate the response to the replacement of hydrogen by a reaction mixture. The absence of an abrupt change in the concentration of methylcyclohexane after catalyst reduction at either 200 or 400°C indicates that, in both cases, toluene entered into the reaction in an adsorbed state. The time taken to attain a steady state after the reduction at 400°C was shorter than that in the former case. This fact is indicative of a decrease in the ability of the catalyst to adsorb toluene after high-temperature reduction.

The response with the dilution $(H_2 + He)/(H_2 + He + C_7H_8)$ exhibited an analogous shape. However, the reverse responses $(H_2 + C_7H_8)/H_2$ and $(H_2 + He + C_7H_8)/(H_2 + He)$ were qualitatively different from one another (Fig. 3b). This is because a maximum in the relaxation curve with a lower concentration of hydrogen corresponds to optimum hydrogen and toluene concentrations on the catalyst surface.

The conclusion that reactive toluene in an adsorbed state found on the catalyst surface was also supported in the responses $(He + C_7H_8)/H_2$ and $(He + C_7H_8)/He/H_2$, which indicated that an amount of toluene remained on the surface after purging the reactor with helium for 3 min (Fig. 3c). This fact suggests that toluene was strongly retained by the catalyst surface. The shape of the curves remained unchanged after catalyst reduction at 400°C; however, the resulting amount of methylcyclohexane decreased.

A comparison between the relaxation curves of the responses $(H_2 + C_7H_8)/H_2$ (Fig. 3b, curve *1*) and $(He + C_7H_8)/H_2$ (Fig. 3c, curve *3*), which were obtained after catalyst reduction at 200°C, demonstrates that the resulting amount of methylcyclohexane in the latter case (in the absence of semihydrogenated species from the catalyst surface) was no lower than that in the former case, when the formation of semihydrogenated species in particular amounts was inevitable. By this is meant that in the hydrogenation of toluene semihydrogenated species occupy a small portion of the catalyst surface. A comparison between analogous responses obtained upon catalyst reduction at 400°C gave the same results.

In the response $D_2/He/(He + C_7H_8)$ with intermediate purging with helium for 60 s, methylcyclohexane was not detected at the reactor outlet; only deuterium-substituted toluenes were formed. By this is meant that a weakly bound, probably, molecular, hydrogen species participates in the formation of methylcyclohexane. Dissociatively adsorbed hydrogen (in this case, deuterium), which is more strongly bound to the surface, cannot hydrogenate toluene; however, it participates in isotope exchange.

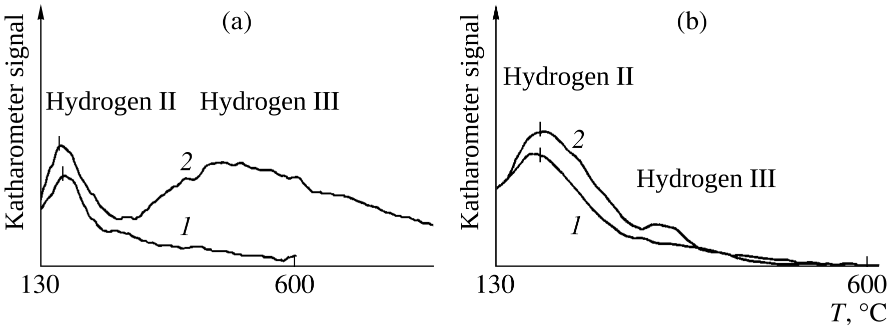

Fig. 4. Hydrogen thermal-desorption curves obtained on (a) Pt/TiO_2 and (b) Pt/SiO_2 catalysts after reduction at (*1*) 200 and (*2*) 500°C.

Figure 3d demonstrates the response $(H_2 + C_6H_6)/H_2$ and the reverse response. They were obtained after catalyst reduction at 200 and 400°C. A comparison of these responses with analogous curves for toluene indicates that the time taken to attain a steady state for benzene was noticeably shorter, whereas they exhibited no qualitative differences from one another. The same result took place in a comparison between other responses with the participation of benzene and the corresponding responses for toluene. This suggests that the mechanisms of benzene and toluene hydrogenation are identical.

Thus, based on non-steady-state studies, we found that the mechanism of benzene or toluene hydrogenation does not depend on the presence of SMSI. In both cases, initial components reacted in adsorbed states; hydrogen reacted as a molecular species, which was weakly bound to the surface. Semihydrogenated species are found on the surface in a relatively low concentration, whereas the reaction occurred in the area of high surface coverages. The effect of SMSI manifested itself in a decrease in the reaction rate, as well as in the amounts of adsorbed reactants, and in a decrease in the strength of binding of the reactants to the catalyst surface. The reaction mechanism of benzene and toluene hydrogenation remained unchanged as the reduction temperature of the Pt/TiO_2 catalyst was increased; that is, it is independent of the presence or absence of SMSI.

The TPD of hydrogen was used for obtaining additional information on the state of adsorbed hydrogen on the catalyst surfaces. This technique allowed us to study the state of strongly bound hydrogen on the catalyst surface. We use the term *strongly bound hydrogen* (hydrogen II and III) to denote the adsorbed hydrogen species that were released only in the course of TPD after purging the reactor with an inert gas for 5 min, as distinct from weakly bound hydrogen (hydrogen I), which was desorbed in an isothermal regime at the temperature of preadsorption (information on this weakly bound hydrogen was obtained using the response technique).

A comparison between the thermal-desorption curves obtained after the reduction of the Pt/TiO_2 (rutile) catalyst at 200 and 500°C (Fig. 4a) demonstrated the presence of a considerable amount of a strongly bound hydrogen species (hydrogen III) on the catalyst surface in the latter case. This species most strongly interacts with the surface of supported metal particles; probably, it dissolves in them and thereby changes the energy characteristics of the surface. It is likely that this decreases the bond strengths of aromatic hydrocarbons and the weakly bound reactive hydrogen species with surface active sites; this was supported by data obtained in non-steady-state studies.

The H_2 TPD curves obtained for the Pt/SiO_2 catalyst indicate that the properties of this catalyst with respect to hydrogen adsorption were different (Fig. 4b). The peak value of hydrogen III did not allow us to assume that processes take place that result in the accumulation of hydrogen on the catalyst surface after the reduction of the catalyst at 500°C.

Thus, based on the above results, we can draw the following conclusions: The kinetics and mechanism of hydrogenation reactions of aromatic hydrocarbons on Pt/TiO_2 catalysts remains unchanged in both the presence and the absence of SMSI. It is likely that the observed effect of a decrease in the catalytic activity of catalysts due to SMSI was attributed to structural changes in active centers and to the presence of strongly bound hydrogen species on the catalyst surface. The results also demonstrate that a complex kinetic approach can be effectively used for the quantitative characterization of SMSI.

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