JOURNAL OF CATALYSIS 74, 207–215 (1982)

Kinetics and Mechanism of Ethane Hydrogenolysis on Silica-Supported Platinum and Platinum–Iron Catalysts

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Received May 8, 1981; revised November 5, 1981

A kinetic analysis of ethane hydrogenolysis has been carried out on Pt/SiO_2 and $PtFe/SiO_2$ catalysts with a wide range of concentration of the components, and with an excess of ethane. With the help of the theory of stationary reactions on heterogeneous surfaces, kinetic equations were obtained describing the reaction rate both in excess hydrogen and excess ethane which are in full agreement with the experimental observations. On platinum in excess hydrogen the rate of hydrogenolysis is determined by the C–C bond rupture of ethane adsorbed in a mildly dissociated C_2H_x form, while in excess hydrocarbon it is determined by the C–C bond rupture of ethane adsorbed in the deeply dissociated form of C_2H_2. The reaction rate passes through a maximum vs ethane pressure at constant hydrogen pressure and vice versa. The formal reaction order in hydrogen and hydrocarbon can be either positive or negative depending on the conditions; the formal power-rate equations may be considered as approximations of the more complicated equations presented in this work.

INTRODUCTION

The hydrogenolysis of aliphatic hydrocarbons was first treated kinetically by Cimino *et al.* (*1*). C–C bond rupture was considered as the rate-determining step, preceded by dissociative adsorption of the hydrocarbon. A simplified version of their equation indeed described the kinetics of the hydrogenolysis of ethane (*2*) and propane (*3*). Later, a modification of the original mechanism made the kinetic equation suitable for describing the change of the hydrogen exponent as the temperature increased, assuming that the first step of the reaction is a dissociative adsorption but not an equilibrium adsorption of ethane (*4–6*).

In studying the hydrogenolysis of hydrocarbons with more than two carbon atoms it was discovered that the rate of hydrogenolysis passes through a maximum as hydrogen pressure increases (*7*). Neither of the kinetic equations mentioned above can be used to explain the maximum in rate as a function of hydrogen pressure. Recently the maximum found for ethane hydrogenolysis on nickel was interpreted by assuming the validity of Langmuir–Hinshelwood kinetics (*8*).

Using a more general theory of the multiple-site adsorption developed by Frennet *et al.* (*9, 10*) hydrogenolysis can be treated kinetically and the resulting equations can describe the maximum for a wide range of hydrogen pressure taking the C–C bond rupture as the rate-determining step. With these equations not only can the maximum with hydrogen pressure be well described (*11*) but also the shift of the rate maximum to higher hydrogen pressure as the carbon number of the hydrocarbon being hydrogenolyzed increases (*12*). Equations developed by Martin and co-workers (*13, 14*) are formally very similar to those mentioned, but the starting point is different as the rate of adsorption is assumed to be rate determining for the hydrogenolysis.

The maximum in rate as a function of hydrogen pressure can also be described by the nonmodified equation of Cimino *et al.*

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0021-9517/82/040207-09$02.00/0

(*1*) assuming it is the C_2H_2 species at which the C–C bond rupture occurs.

However, the above-mentioned equations are not adequate to explain the maximum in rate vs hydrocarbon pressure when a reaction is investigated in a wide-enough pressure range (*15*). Although a more general equation was applied by Mao *et al.* for the dehydrogenation of *n*-pentane (*15*) and by Kiperman and co-workers for the hydrogenolysis and isomerization of *n*-pentane (*16, 17*) the mechanism is not fully revealed in the kinetics.

The main goal of the present study is to show for ethane hydrogenolysis how the kinetic equations derived represent the effect due to the variations of hydrogen and hydrocarbon pressure over a wide range. The main concept of the work is to take into account different degrees of hydrogen loss of the ethane molecule on the surface, depending on the experimental conditions, and to evaluate its consequence for the kinetic equations.

EXPERIMENTAL

Experiments were carried out in a circulation apparatus with a reaction volume of 0.182 liter. Ethane of "puriss" grade was obtained from Fluka. Hydrogen was purified by diffusion through a silver–palladium thimble.

Two types of silica-supported catalyst were used, namely, pure platinum with a 1.1 wt% metal content, and platinum–iron with 1.1 wt% Pt and 0.7 wt% Fe. The preparation, pretreatment, and catalyst characteristics were detailed earlier (*18*). Between runs catalysts were treated by one of the following methods. The first one comprised evacuation of the catalyst at the experimental temperature for 30 min, circulation of oxygen at a pressure of about 0.7 kPa for 15 min, evacuation for 15 min, and finally reduction with hydrogen at a pressure of about 7 kPa for 1 hr followed by evacuation for 30 min. In the second method the oxygen treatment was omitted.

Reaction products were analyzed by GC supplied with FID, periodically extracting samples of 0.5 cm^3 from the reaction volume. Separation of methane and ethane was carried out at 353 K on a 1-m-long column filled with alumina.

The experiments were carried out in the temperature range 523–623 K while changing the partial pressure of ethane from 0.4 to 21.7 kPa and that of hydrogen from 0.2 to 10.3 kPa. The ratio of ethane and hydrogen changed in this case from 0.1 to 37.

For the kinetic calculations values of the initial rate (r_0) of hydrogenolysis were calculated from the methane formation extrapolated to zero time using linear regression.

RESULTS

In Table 1 the kinetic data obtained for $PtFe/SiO_2$ catalyst treated according to the first method, i.e., oxidation–reduction, can be seen. Table 2 shows the corresponding results for Pt/SiO_2 catalyst treated only with hydrogen, i.e., according to the sec-

TABLE 1

Dependence of Ethane Hydrogenolysis Rate on the Composition of the Reaction Mixture on Platinum–Iron Catalyst Treated with Oxygen and Hydrogen

$P_{C_2H_6}$ (kPa)	P_{H_2} (kPa)	$\frac{P_{C_2H_6}}{P_{H_2}}$	Reaction rate (μmol) $g_{cat}^{-1} \cdot s^{-1}$)		
			Exp.	Calcd. by Eq. (4)	Calcd. by Eq. (5)
1.31	10.34	0.13	0.00068	0.00082	
1.31	5.71	0.23	0.00165	0.00178	
1.31	4.48	0.29	0.00268	0.00241	
1.26	3.63	0.35	0.00337	0.00300	
1.28	2.68	0.48	0.00399	0.00421	
0.62	1.16	0.53	0.00673	0.00679	
1.14	1.20	0.95	0.00866	0.00838	
2.03	1.21	1.68	0.00885	0.00893	
3.29	1.22	2.71	0.00748	0.00832	
3.32	1.18	2.80	0.00858	0.00840	0.00672
4.50	1.19	3.79	0.00723	0.00755	0.00728
5.67	1.19	4.77	0.00764	0.00681	0.00744
1.14	0.21	5.55	0.00439		0.00424
9.73	1.19	8.20	0.00697		0.00710
10.24	1.12	9.14	0.00696		0.00694
13.09	1.11	11.81	0.00654		0.00630
19.40	1.23	15.74	0.00521		0.00564

Note. Temperature, 573 K. All rates are determined in separate runs.

TABLE 2

Dependence of Ethane Hydrogenolysis Rate on the Composition of the Reaction Mixture on Platinum Catalyst Treated Only with Hydrogen

Temp. (K)	$P_{C_2H_6}$ (kPa)	P_{H_2} (kPa)	$\frac{P_{C_2H_6}}{P_{H_2}}$	Reaction rate (μmol $g_{cat}^{-1} \cdot s^{-1}$)		
				Exp.	Calcd. by Eq. (4)	Calcd. by Eq. (5)
523	1.59	3.63	0.44	0.000038	0.000070	
	1.67	3.11	0.54	0.000079	0.000091	
	1.96	1.64	1.19	0.000255	0.000241	
	1.62	0.67	2.44	0.000711	0.000592	
	1.69	0.57	2.97	0.000653	0.000710	
	3.41	1.12	3.03	0.000414	0.000513	0.000304
	3.41	0.64	5.29	0.000831	0.000813	0.001010
	3.88	0.59	6.63	0.001055	0.000874	0.001187
	6.09	0.59	10.27	0.001539		0.001289
	6.64	0.62	10.49	0.001372		0.001254
	9.03	0.50	18.05	0.001130		0.001264
	15.14	0.51	29.61	0.001047		0.001030
573	0.68	7.09	0.10	0.00038	0.00062	
	0.68	2.37	0.29	0.00222	0.00252	
	2.36	4.07	0.58	0.00297	0.00286	
	2.21	2.26	0.98	0.00494	0.00455	
	1.18	1.13	1.04	0.00677	0.00650	
	0.58	0.33	1.77	0.01202	0.01240	
	1.71	0.66	2.58	0.00837	0.00816	0.00749
	2.36	0.51	4.60	0.01327	0.00734	0.01336
	3.49	0.59	5.92	0.01163		0.0258
	8.13	0.60	13.54	0.01374		0.01303
	10.96	0.58	18.78	0.01148		0.01214
	21.72	0.59	37.16	0.00943		0.00888
623	0.41	4.03	0.10	0.0725	0.0658	
	0.65	1.84	0.35	0.0972	0.1073	
	1.14	1.08	1.05	0.1018	0.0854	
	0.76	0.52	1.47	0.0822	0.0978	0.0900
	1.50	0.71	2.11	0.0739	0.0629	0.0722
	1.88	0.59	3.16	0.1065		0.0988
	3.13	0.36	9.32	0.0765		0.0790

ond method. The data obtained on PtFe/SiO_2 catalyst regenerated with hydrogen treatment are presented in Table 3.

It is important to note that the reaction rate passes through a maximum when the pressure of either hydrogen or ethane increases keeping the second component constant. This is indicated in Figs. 1 and 2 where the date obtained on PtFe/SiO_2 catalyst regenerated by the first method are presented.

To check the effect of the reaction product, CH_4, on the rate of hydrogenolysis, an experiment was carried out in which methane was introduced to the initial mixture in a quantity three times greater than that formed normally during the reaction. In this case the initial rate determined by the slope of the conversion curve did not show any change, as can be seen in Fig. 3, i.e., the reaction is not inhibited by methane. The slight deviation of the curves at high conversion can probably be explained by the different conditions of the reversible deactivation of the catalyst due to coke formation.

In a special series of experiments with standard mixtures on Pt/SiO_2 catalyst the temperature dependence of the hydrogenolysis rate was checked separately using mixtures with ethane excess ($C_2H_6 : H_2 = 3 : 1$) and with hydrogen excess ($C_2H_6 : H_2 = 1 : 12$). The results of these experiments are presented in Table 5.

DISCUSSION

The available literature data (*6, 19*) allow us to assume that during ethane hydrogenolysis the first step is its dissociative adsorption. The adsorbed ethane, depending on the nature of the catalyst and on the experimental conditions, can lose some of its hydrogen atoms (*19*). The rate-determining step of the reaction is apparently C–C bond rupture (*19*) which can occur at different degrees of dehydrogenation of the adsorbed hydrocarbon. The successive methane formation and its desorption must proceed rapidly (*20*), as is supported by the absence of a methane effect on the reaction rate (Fig. 3).

It is assumed that in excess hydrogen reaction route I (see below) is operative, where the C–C bond rupture occurs in ethane adsorbed in the form of $*C_2H_5$, where $*$ means the active centre of the catalyst.

When ethane is present in excess, its dehydrogenation proceeds more deeply in the adsorbed state before C–C bond rupture occurs. Generally speaking, the formation of all species is possible until nearly all hydrogen atoms of ethane have been lost. However, we confine ourselves to investigating the formation and decomposition of C_2H_2 species (route II), since for platinum the interaction promoting the formation of more dehydrogenated structures is least characteristic as compared to other metals of Group VIII.

1. $H_2 + 2* = 2\underset{*}{H}$
2. $C_2H_6 + 2* = \underset{*}{C_2H_5} + \underset{*}{H}$
3. $\underset{*}{C_2H_5} + * = \underset{*}{CH_3} + \underset{*}{CH_2}$
4. $\underset{*}{CH_2} + \underset{*}{H} = \underset{*}{CH_3} + *$
5. $\underset{*}{CH_3} + \underset{*}{H} = CH_4 + 2*$

Route I

1. $H_2 + 2* = 2\underset{*}{H}$
2. $C_2H_6 + 2* = \underset{*}{C_2H_5} + \underset{*}{H}$
3. $\underset{*}{C_2H_5} + * = \underset{*}{C_2H_4} + \underset{*}{H}$
4. $\underset{*}{C_2H_4} + * = \underset{*}{C_2H_3} + \underset{*}{H}$
5. $\underset{*}{C_2H_3} + * = \underset{*}{C_2H_2} + \underset{*}{H}$
6. $\underset{*}{C_2H_2} + * = 2\underset{*}{CH}$
7. $\underset{*}{CH} + \underset{*}{H} = \underset{*}{CH_2} + *$
8. $\underset{*}{CH_2} + \underset{*}{H} = \underset{*}{CH_3} + *$
9. $\underset{*}{CH_3} + \underset{*}{H} = CH_4 + 2*$

Route II

In accordance with the above statements, in route I the rate-determining step must be step 3, while in route II it is step 6. The others can be considered fast steps. It is further assumed that the reaction takes place in a real adsorbed layer. In such cases, in accordance with the theory of stationary reactions on heterogeneous surfaces (*21*), the reaction rate via route I (where hydrogen is in excess on the surface) will be equal to that of the rate-determining step 3 and can be described by the

TABLE 3

Dependence of Ethane Hydrogenolysis Rate on the Composition of the Reaction Mixture on Platinum–Iron Catalyst Treated Only with Hydrogen

$P_{C_2H_6}$ (kPa)	P_{H_2} (kPa)	$\frac{P_{C_2H_6}}{P_{H_2}}$	Reaction rate (μmol $g_{cat}^{-1} \cdot s^{-1}$)	
			Exp.	Calcd. by Eq. (4)
0.58	2.30	0.25	0.000216	0.000320
1.27	4.00	0.32	0.000315	0.000289
0.77	2.33	0.33	0.000295	0.000389
1.32	2.26	0.58	0.000462	0.000559
1.26	1.29	0.98	0.001095	0.000916
3.22	2.30	1.39	0.000766	0.000743
3.82	2.30	1.66	0.000881	0.000756
1.32	0.51	2.61	0.001494	0.001571
6.87	2.34	2.94	0.001196	0.000713

Note. Temperature 573 K.

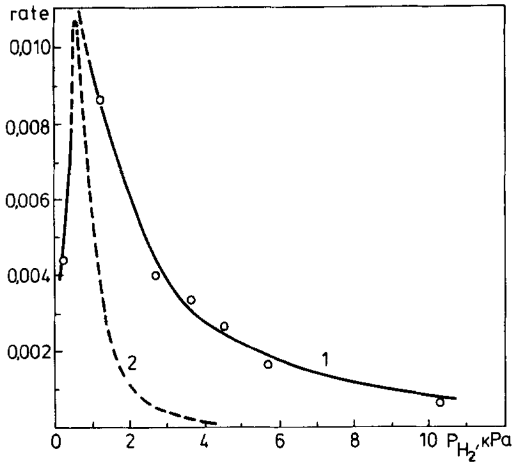

FIG. 2. Dependence of ethane hydrogenolysis rate on the pressure of hydrogen at constant ethane pressure of about 1.3 kPa. Catalyst PtFe/SiO$_2$, temperature 573 K. Curve 1 is plotted according to Eq. (4), curve 2 according to Eq. (5).

equation

$$r_1 = \frac{k_3' p_{C_2H_5}}{D^{2\alpha}}, \tag{1}$$

where $D = \Sigma a_i p_i$, i.e., the sum of products of the adsorption equilibrium constants a_i (on the most strongly adsorbing sites) and the values of the virtual pressure, p_i, of the adsorbed layer of the corresponding species. k_3' stands for the rate constant of step 3 and α means the coefficient of linearity ratio which in the given case can be considered near to unity (full coverage by the adsorbed species).

Due to the fact that the adsorption of methane is considerably weaker than that of ethane (*20*) and that it has no influence on the reaction rate, the virtual pressures

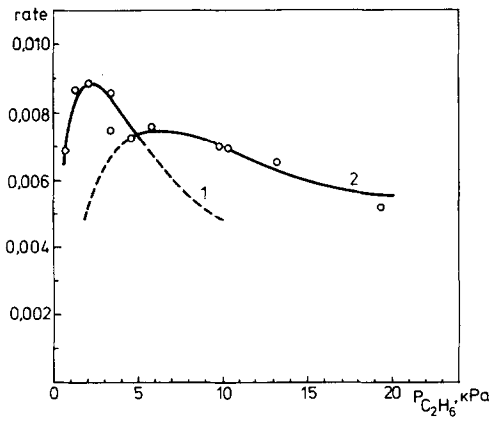

FIG. 1. Dependence of ethane hydrogenolysis rate on the pressure of ethane at a constant hydrogen pressure of about 1.2 kPa. Catalyst PtFe/SiO$_2$, temperature 573 K. Curve 1 is plotted according to Eq. (4), curve 2 according to Eq. (5).

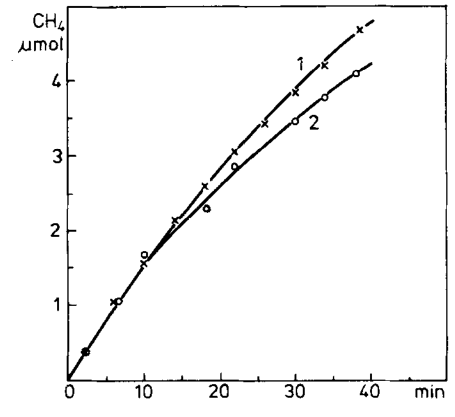

FIG. 3. Change of methane concentration in the reaction system in a standard experiment and in an experiment with methane addition in the initial mixture. Catalyst Pt/SiO$_2$, temperature 573 K. Composition of the mixture in micromoles: (1) $P_{C_2H_6} = 120.8$, $P_{H_2} = 46.7$; (2) $P_{C_2H_6} = 119.3$, $P_{H_2} = 47.7$, $P_{CH_4} = 14.0$.

for CH_2 and CH_3 species can be neglected. The remaining two summands in the denominator of Eq. (1) can be expressed by the rapid equilibrium of steps 1 and 2:

$$P_H = K_1 P_{H_2}^{0.5}, \tag{2}$$

$$P_{C_2H_5} = \frac{K_2}{K_1} \frac{P_{C_2H_6}}{P_{H_2}^{0.5}}, \tag{3}$$

where K_1 and K_2 are the equilibrium constants of the corresponding steps, and P_{H_2} and $P_{C_2H_6}$ are the hydrogen and ethane pressures in the gas phase, respectively.

In this way with excess hydrogen on the surface the reaction rate can be described by the equation

$$r = \frac{k_1 P_{C_2H_6} P_{H_2}^{0.5}}{(P_{C_2H_6} + k_2 P_{H_2})^2}, \tag{4}$$

where $k_1 = k_3' K_1/a_1^2 K_2$ and $k_2 = a_2 K_1^2/a_1 K_2$.

If hydrogen is present in the system in a small quantity and hydrocarbon predominates on the surface the reaction rate will be determined by route II; using similar considerations as in the previous case we come to the equation

$$r = \frac{k_3 P_{C_2H_6} P_{H_2}{}^2}{(P_{C_2H_6} + k_4 P_{H_2}^{2.5})^2}, \tag{5}$$

where $k_3 = k_6' K_1^4/a_1^2 K_2 K_3 K_4 K_5$ and $k_4 = a_2 K_1^5/a_1 K_2 K_3 K_4 K_5$.

The constants k_1 and k_3 are proportional to the rate of the corresponding slow step (steps 3 and 6 accordingly); constants k_2 and k_4 correspond to the ratio of adsorption coefficients of hydrogen and ethane (in the form C_2H_5 or C_2H_2 accordingly).

It turns out that the reaction rate cannot be described by a single equation in the whole $P_{C_2H_6}/P_{H_2}$ range. Simultaneously if it is accepted that in excess hydrogen the reaction proceeds via route I [Eq. (4)], and in excess hydrocarbon via route II [Eq. (5)], a good agreement is found between the calculated and the experimental values. Calculation was carried out by a nonlinear weighted least-squares method using a Gauss–Newton iteration. The computed values by the equations are presented in the last columns of Tables 1–3. The values of the constants for which the best fit can be obtained are presented in Table 4 along with the values of the mean square errors. From these values it is concluded that the oxygen–hydrogen treatment of the catalyst considerably increases the accuracy of the experiments as it improves the stability of the catalyst.

It can be seen from Figs. 1 and 2 and Table 1 that in the case when $P_{C_2H_6}/P_{H_2}$ ratios are less than 4, experimental points are in good agreement with the theoretical values calculated according to Eq. (4), and for higher ratios with those corresponding to Eq. (5). An analogous phenomenon can be observed for the Pt/SiO_2 catalyst after its treatment only with hydrogen (Table 2). With increasing temperature the validity range of Eq. (4) to that of Eq. (5) is shifted approximately from $P_{C_2H_6}/P_{H_2} = 3$–3.5 at 523 K to $P_{C_2H_6}/P_{H_2} = 1$–1.5 at 623 K.

Experiments on the $PtFe/SiO_2$ catalyst after its treatment only with hydrogen were carried out at $P_{C_2H_6}/P_{H_2} < 3$. Here all of the data obey Eq. (4). The difference between the experimental and calculated values in the last row of Table 3 [row 9, $P_{C_2H_6}/P_{H_2} = 2.94$] can probably be explained by the fact that at this pressure ratio Eq. (5) has already started to operate.

The analysis of data in Tables 1 and 2 shows that the range of shift from the reaction proceeding mainly according to route I to that proceeding mainly by route II seems to be narrow. The indicated two stationary states can therefore be considered as the fundamental ones for ethane hydrogenolysis on platinum.

Having compared Tables 1, 2, and 3 it can be concluded that neither iron addition to the catalyst nor the alteration of the treatment conditions can change the mechanism of the reaction: in each case it is described by the routes presented above from which Eqs. (4) and (5) can be derived. This conclusion coincides with the one drawn earlier (*18*) based on the comparison

TABLE 4

Calculated Values of Coefficients in Eq. (4) and (5)

Catalyst and treatment	Constants			
	k_1 (μmol · kPa$^{0.5}$ · g$_{cat}^{-1}$ · s^{-1})	k_2	k_3 (μmol · kPa^{-1} · g$_{cat}^{-1}$ · s^{-1})	k_4 (kPa$^{-1.5}$)
Pt–Fe/SiO_2, O_2 + H_2, 573 K	0.063 ± 0.004	1.61 ± 0.1	0.12 ± 0.011	3.38 ± 0.36
Pt/SiO_2, H_2, 523 K	0.019 ± 0.009	7.23 ± 2.49	0.11 ± 0.025	26.8 ± 5.7
Pt/SiO_2, H_2, 573 K	0.042 ± 0.004	1.49 ± 0.16	0.91 ± 0.097	22.0 ± 2.2
Pt/SiO_2, H_2, 623 K	0.137 ± 0.026	0.22 ± 0.06	2.91 ± 0.54	9.4 ± 1.5
Pt–Fe/SiO_2, H_2, 573 K	0.011 ± 0.004	2.24 ± 0.7	—	—

of the data for isotope exchange and ethane hydrogenolysis. Furthermore, iron addition or alteration of regeneration have practically no effect on the value of the constant k_2 (Table 4). In other words, the ratio of the adsorption coefficients of hydrogen and ethane remains practically unchanged if the latter is adsorbed in the form of C_2H_5. At the same time iron addition brings about a considerable decrease of the constant k_4, i.e., it promotes ethane adsorption in the form of C_2H_2. The switch between routes I and II from $P_{C_2H_6}/P_{H_2} \approx 4$ for Pt/SiO_2 catalyst to $P_{C_2H_6}/P_{H_2} \approx 2$ for PtFe/SiO_2 catalyst at 573 K corresponds to this (see Tables 2 and 3). Physically this means that on iron–platinum catalyst ethane is adsorbed in a deep dehydrogenation stage at lower C_2H_6/H_2 ratio.

The constants k_2 and k_4 tend to decrease with increasing temperature. This means that the adsorption of hydrogen is diminished compared to that of any form of ethane when temperature is enhanced. In this sense iron addition to platinum has the same effect on the catalyst as does temperature increase. The shift of the location of the rate maximum vs ethane pressure towards lower ethane pressure as temperature increases also corresponds to the decrease of k_2 and k_4.

The kinetic equations accepted in Refs. (*12, 16, 17*) cannot be used in our case as they do not make it possible to describe how the reaction rate passes through a maximum with increase of ethane pressure. It should be noted that in those works all the experiments were carried out only in considerable hydrogen excess.

The maximum of the reaction rate vs hydrogen during the hydrogenolysis of different hydrocarbons has been observed earlier (*20*). The shift of this maximum as temperature is changed [observed for butane (*22*)] is a result of the change of constants in the denominator of equation type (4) or (5), i.e., it is the result of the change of the hydrogen-to-hydrocarbon ratio on the surface.

In the literature there are many contradictions concerning the apparent activation energy of the hydrogenolysis. All these discrepancies are mainly due to the experimental conditions under which the activation energy was determined. According to the data presented in Table 5 the apparent energy of activation depends on the composition of the reactants: in hydrogen excess

TABLE 5

Dependence of Ethane Hydrogenolysis Rate on Temperature on Pt/SiO_2 Catalyst Treated Only with Hydrogen

Temp. (K)	$P_{C_2H_6}$ (kPa)	P_{H_2} (kPa)	Rate (μmol $g_{cat}^{-1} \cdot s^{-1}$)	Apparent energy of activation (kJ/mol)		
				Exp.	Calculated	
					Eq. (4)	Eq. (5)
548	0.86	0.29	0.0072			
573	0.90	0.30	0.0188	98	—	108
598	0.90	0.30	0.0440			
548	0.43	5.13	0.00027			
573	0.43	5.13	0.00222	194	226	—
598	0.42	5.05	0.00929			

194 kJ/mol, in ethane excess 98 kJ/mol were measured. On the basis of the values of the constants of Eqs. (4) and (5) (see Table 4) and the actual hydrogen and hydrocarbon pressures, the values of the energy of activation were calculated by Eqs. (4) and (5). The obtained values are in quite good agreement with the experimental ones (Table 5). For comparison it is noted that on Pt/SiO_2 catalyst (treated with oxygen and hydrogen) in hydrogen excess ($P_{C_2H_6}/P_{H_2}$ = 1 : 10) a value of about 230 kJ/mol was obtained (*18*).

CONCLUSIONS

It is shown by the kinetic analysis detailed above that the mechanism of hydrogenolysis does not depend on the type of the catalyst and its treatment to a large extent. However, depending on the conditions of the process its rate can be described by different kinetic equations corresponding to different routes of the reaction. In excess hydrogen on the catalyst surface the C–C bond rupture of ethane adsorbed in a mildly dissociative form (cf. C_2H_5) has a decisive role, and the reaction rate can be described by Eq. (4). In excess hydrocarbon the dissociation of the adsorbed ethane is deeper and the C–C bond rupture occurs in the form of C_2H_2; Eq. (5) then describes the rate. The real process seems to proceed in other stationary states as well, the C–C bond rupture occurring at different levels of dehydrogenation of the hydrocarbon residue, but the indicated two states corresponding to routes I and II are the most important.

It can be assumed that similar dependences are valid in the hydrogenolysis of other hydrocarbons as well, and also on other catalysts. However, the decisive role in these or other circumstances is played by the splitting of species with different hydrogen contents.

ACKNOWLEDGMENT

The authors are indebted to Dr. L. Naszódi for help in fitting the data.

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