INVESTIGATION OF HYDROGENATION IN LIQUID PHASE. XX.*
DIFFUSION OF HYDROGEN IN INTERNAL PORES OF THE CATALYST GRAIN

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The influence of the catalyst grain size and of the temperature on the hydrogenation of cyclohexene was studied in methanol, hexane and benzene in the presence of a palladium catalyst (Pd on active carbon) and in tetrachloromethane on a platinum catalyst (Pt on silica gel). It was established that in the case of a high value of the reaction rate or the catalyst activity the catalyst inner surface need not be totally utilized during the reaction even at the minimum granulation employed. From the experimental results, the value of the activation energy of the hydrogen diffusion was determined for all solvents used.

The problem of the diffusional mass transfer in internal pores of a catalyst (so-called internal diffusion) during catalytic reactions in the gaseous phase was solved by many authors, basic works in this field were summarized for example by Satterfield and Sherwood[1]. There are only few works[2-6] dealing with the study of the internal diffusion of the reaction components during the catalytic hydrogenation in the liquid phase. It is caused by the complexity of the reaction system containing three phases necessarily in a mutual contact during the reaction: solid (a porous catalyst), liquid (a hydrogenated substrate, eventually a substrate dissolved in a certain solvent), and gaseous ones (hydrogen). A perfect contact of all three phases of the system is usually stipulated by an intensive agitation of the whole reaction space. It was shown in a previous work[6] that such a turbulence in the reactor could be reached at which the reaction rate did not depend on the agitation intensity. At such conditions, the measured reaction rate may be affected only by the diffusional transfer of the reaction components in internal pores of the catalyst grain. Satterfield, Ma, and Sherwood[2,3] studied the dependence of the hydrogenation rate of α-methyl styrene on the dispersity of a palladium catalyst (0·5 wt.% Pd on Al_2O_3) and on temperature. They found that it was possible to apply for the description of the mass transfer in the catalyst grain the relations hitherto used for reactions proceeding in the gaseous phase with the rate of the whole process governed in the first place by the diffusion of hydrogen dissolved in the liquid reaction phase and not by that of a hydrogenated substrate. An explanation of this fact may be that the hydrogen concentration in the liquid phase is usually by several orders less than that of the substrate. Nahas[4] occupied himself with the influence of the catalyst grain size on a high pressure hydrogenation of isopropylbenzene on a nickel catalyst, but he was only supposing that the inner surface of the catalyst had been utilized totally at the minimum granulation.

THEORETICAL

The hydrogenation of unsaturated compounds in the liquid phase may be thought of as an irreversible bimolecular reaction $(A + B \rightarrow R)$, so that during a study of the internal diffusion of the reaction components (hydrogen and a substrate) in catalyst grain pores it is inevitable to define conditions when it is necessary to consider the braking effect of the diffusion of both reaction components on the reaction rate or when it suffices to consider the simplified monomolecular system.

Maymò and Cunningham[7] studied the influence of the ratios of the diffusion coefficients and concentrations of the reaction components on the dependence of the effectiveness factor of the catalyst on the Thiele modulus for a bimolecular reaction system. From their results it follows that it is possible to take the system studied for a pseudomonomolecular one with an error less than 10% when the following condition is satisfied:

$$y = (C_B D_B)/(C_A D_A) > 2 . \tag{1}$$

B denotes the reaction component which is present in excess or which exhibits a higher value of the diffusion coefficient.

During the hydrogenation at an atmospheric pressure is the concentration of hydrogen dissolved in the reaction mixture substantially lower than that of the substrate (component B); however, it is obvious that the diffusion coefficient of hydrogen is higher than that of the substrate due to the molecule size, so that an examination of a system studied with respect to Eq. (1) may be performed unambiguously only on the basis of the knowledge of all quantities present.

In Table I all necessary data are summarized for the systems studied in this work (for the sake of simplicity it was assumed that the properties of the reaction mixture were identical with those of the pure solvents as the concentration of the substrate,

TABLE I

Diffusion Coefficients, Concentrations of Dissolved Hydrogen and Values of the Parameter y for the Solvents Studied

T 298 K; P_b 740 Torr; C_S 3·80 . 10^{-4} mol cm^{-3}.

Solvent	$C_H 10^6$ mol cm^{-3} (see[21-23])	$D_H 10^0$ cm^2 s^{-1} (see[8])	$D_S 10^5$ cm^2 s^{-1}	y
Benzene	2·61	20·2	2·17 [9]	15·6
Hexane	3·84	62·4	4·14 [9]	6·6
Methanol	3·04	17·2[a]	(2)	(14·5)
Tetrachloromethane	2·73	9·87	1·28 [10]	18·2

[a] $T = 293$ K.

i.e. of cyclohexene, was as low as c_s $3.8 . 10^{-4}$ mol cm^{-3} during the measurements). Up to this time there is only few diffusion coefficients for different liquid systems in the literature. With respect to the fact that no data were found for the diffusion of cyclohexene in the solvents employed, it was assumed that the values of the diffusion coefficients of cyclohexene and cyclohexane[8-10] in benzene, hexane, and tetrachloromethane were identical whereas for methanol a probable value was taken (Table I) estimated from the hitherto published data[9,11]. From the given values of the quantity y it is obvious that Eq. (1) is satisfied quite well for the systems studied in all cases, so that it is possible to accept a statement that the measured rate is governed by the hydrogen diffusion in internal pores of the catalyst. The systems may be thus treated as pseudomonomolecular ones with the reaction order with regard to hydrogen equal to unity and the concentration of the substrate in the porous substance as a constant. This conclusion is in accordance with other works[2,3].

The effectiveness factor η of the inner surface of spherical particles of the catalyst, in which an irreversible isothermal reaction of the first order proceeds, is a function of the Thiele modulus Q according to the relation[1]:

$$\eta = (k/k_0) = (3/Q^2)\left[Q \operatorname{cotgh}(Q) - 1\right] . \tag{2}$$

The Thiele modulus Q may be expressed by the relation (for the pseudozeroth order of the reaction with regard to the substrate):

$$Q = (d_p/2)\sqrt{(k_0\, a/D_{eff})} . \tag{3}$$

The effective diffusion coefficient D_{eff} is defined by [12]:

$$D_{eff} = D\Theta/\tau . \tag{4}$$

These relations were used in our work for evaluating the experiments with the crushed catalyst of an irregular shape. The value of the Thiele modulus as well as the effectiveness factor of the catalyst depends for the chosen reaction and for the catalyst employed also on temperature. The temperature dependence of the hydrogenation rate constant and of the diffusion coefficient may be expressed by the relations:

$$k_0 = A_k \exp\left(-E_k/RT\right) , \tag{5}$$

$$D = A_D \exp\left(-E_D/RT\right) . \tag{6}$$

Gupta and Douglas[13] proposed for the influence of the diffusion of the reaction components in catalyst pores on the values of the apparent activation energy E

$$E = \left[E_k(2 + \psi) - E_D\psi\right]/2 \tag{7}$$

with $$\psi = d \ln \eta / d \ln Q .$$

In the region of a strong influence of the internal diffusion, the effectiveness factor of the catalyst is equal to:

$$\eta = (6/d_p) \sqrt{(D_{eff}/k_0 a)} \qquad (8)$$

and the quantity ψ reaches the value of -1, so that the apparent activation energy may be expressed by the relation:

$$E = (E_k + E_D)/2 . \qquad (9)$$

This relation was verified experimentally[2,3]. A possibility arises to make use of Eq. (9) for the experimental determination of the activation energy of the molecular diffusion of hydrogen in liquids employable either as a substrate or as a solvent during the catalytic hydrogenation in the liquid phase. The determination of this quantity for some solvents was one of the main purposes of this study.

EXPERIMENTAL

Chemicals and Catalysts

Cyclohexene was prepared by the dehydration of cyclohexanol on γ-alumina[14], n.b.p. 82—83°C. Before the actual measurement it was purified[15] from peroxides which inactivate the catalyst due to a strong adsorption. The following commercial reagents were used: benzene (pure grade, thiophene free, Lachema), n.b.p. 80·0°C. Hexane (a.r. grade, Lachema), n.b.p. 68·7°C. Methanol (a.r. grade, Lachema), n.b.p. 64·8°C. Tetrachloromethane (a.r. grade, Lachema), n.b.p. 76·5°C. Hexachloroplatinic acid (a.r. grade, Safina, Vestec). Silicagel (precipitated, Sintezspirt Ufa, USSR), beads of the diameter 4—5 mm. Hydrogen (technical B electrolytic grade, Technoplyn, Pardubice) was catalytically purified before the use at 180°C on Ni/SiO_2 (Czechoslov. Pat. 111 791) and Cu/SiO_2 (Czechoslov. Pat. 91 868) catalysts.

Catalyst I (No 9041, Chem. Závody, Záluži) 3 wt.% Pd on narrow pore active carbon cylinders (diameter 4·2 mm). *Catalyst* II: 10 wt.% Pt on silica gel. A methanol solution of hexachloroplatinic acid was added to silicagel. The solvent was evaporated during a thorough mixing and the dry residue was heated to 100°C for 2 hours. The it was annealed in a furnace at 550°C for 1 hour. The physical properties of the catalysts employed:

Catalyst	Sp. surface $m^2 g^{-1}$	Density $g cm^{-3}$	Porosity
I (3% Pd/C)	1 234	2·25	0·462
II (10% Pt/SiO$_2$)	265	2·20	—

The specific surface and porosity of the catalyst I were taken from another work[5]. The specific surface of the catalyst II was determined by a chromatographic method[16], the density of the catalysts was established pycnometrically. Both catalysts were crushed and the necessary frac-

tions of different granulations were obtained by screening. The respective particle size was taken as the arithmetic mean of the diameters of two neighbouring screens. Besides that, the mesh fraction of the finest screen was obtained (less than 0·04 mm), the dispersity of which was determined in the case of the catalyst I by Andreasen's sedimentation apparatus[17]. The catalyst II was used only for the experiments with tetrachloromethane as the hydrogenation of cyclohexene in this solvent on the catalyst I did not proceed with an observable rate. In the case of the remaining solvents, *i.e.* methanol, benzene, and hexane, was the activity of the catalyst I sufficient. Benzene could be used as a solvent for the hydrogenation of cyclohexene because it was not hydrogenated on the palladium catalyst I.

Apparatus

The measurement was performed in the apparatus employed for the study of hydrogenation reactions in the liquid phase[18] at a constant hydrogen pressure and temperature. The reaction rate was determined from decrease of the hydrogen volume in gasometric burettes connected to the reactor. The glass discontinuous reactor[19] equipped with a thermostating jacket was fixed in a shaker making it possible to change continuously the agitation frequency (0—1 300 swings/min). The measurement in all experiments was performed in the kinetic region with respect to the diffusional transfer of the reaction components outside the catalyst grain, *i.e.* at such hydrodynamical conditions in the reactor for which the reaction rate did not depend on the agitation intensity[6]. For the measurements with large (noncrushed) catalyst grains, a cylindrical strainer basket was placed into the reactor neck, whose location in the reactor space see Fig. 1. The strainer basket prevented great catalyst particles from abrading by the reactor walls during its shaking in the course of the actual reaction.
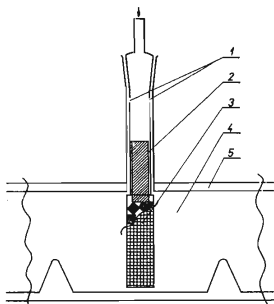

Fig. 1

Fixation of the Strainer Basket in the Reactor Neck

1 Hydrogen inlet; *2* helical coupling; *3* strainer basket; *4* reaction space; *5* thermostated jacket.

Operation Procedure

The kinetic measurements were performed at an atmospheric pressure in the temperature range 15—35°C with the thermostating accuracy of ±0·1°C. The catalyst was placed into the reactor (its weight was in most experiments 0·06—0·1 g; in the case of the noncrushed catalyst 0·4—0·5 g) followed by 25 ml of the solvent. After washing the apparatus with hydrogen, checking on the tightness of the whole system, and activating the catalyst, 1 ml cyclohexene was added into the

reactor and the measurement of the reaction rate began. The reaction rate was determined from decrease of the hydrogen volume read off on gasometric burettes in 5 minutes intervals. The values of the initial reaction rates were read off from the time dependence of the reaction rate. The error of a single reaction rate constant determination was 5—7 relative % and it was compensated by a greater number of experiments at the given conditions. Each measurement was repeated at least three times. The reaction was of the zeroth order with regard to cyclohexene for the experiments with the catalyst II in tetrachloromethane and with the catalyst I in benzene. In the case of the remaining solvents and of the catalyst I, the reaction order with respect to cyclohexene was approximately equal to unity.

Calculation of the Reaction Rate

The reaction was considered to be of the first order with regard to hydrogen[5], so that the initial reaction rate r_0 could be expressed by the relation:

$$r_0 = k C_H . \tag{10}$$

The hydrogenation rate constant k included the initial concentration of the substrate if the reaction order with respect to the substrate was different from zero. The concentration C_H of hydrogen dissolved in the reaction mixture at an experimental temperature T was calculated from the expression:

$$C_H = C'_H \left(\frac{P_b - P^0}{760} \right) \exp \left[\frac{\Delta H}{R} \left(\frac{1}{T'} - \frac{1}{T} \right) \right] . \tag{11}$$

The saturated vapour pressures P^0 of the reaction mixture were taken from the literature[20]. In all cases it was assumed that the liquid phase properties were identical with those of the pure solvents due to low concentrations of the hydrogenated substrate in the reaction mixture. The hydrogen solubility in the solvents was taken from the literature[21-23]. The heat of solution of hydrogen in the liquids was determined from the temperature dependences of the tabulated data. Only in the case of hexane for which a single value at one temperature was accessible[23], the heat of solution of hydrogen in heptane and octane was used[22], which is the same in these two liquids. Thus, it was supposed that in the aliphatic hydrocarbon series the value of this quantity is a constant.

RESULTS AND DISCUSSION

In the first stage of our work, the influence of the catalyst grain size on the rate constant of the hydrogenation of cyclohexene at 25°C was followed (Fig. 2). It is evident that during the experiments on the palladium catalyst I (i.e. in the case of benzene, hexane, and methanol) both the kinetic and diffusion regions were reached from the point of view of the internal mass transfer in the catalyst pores in the granulation range employed. With respect to the fact that the platinum catalyst II was more active (the solvent employed was only tetrachloromethane) than the palladium catalyst I, the kinetic region was hard to attain in these experiments; the effectiveness factor of the catalyst at the finest granulation (d_p 2 . 10^{-3} cm) reached a value of 0·75. Analogous dependences were obtained at other temperatures.

Therefore it follows from the results that during studies of the kinetics or mechanism of the hydrogenation in the liquid phase, the use of a fine catalyst granulation is not a sufficient guarantee for measuring in the kinetic region from the point of view of the internal diffusion. In every case it is suitable to make oneself sure that the kinetic region has been reached by using at least two different catalyst granulations. The values of the hydrogenation rate constants k_0 at a complete utilization of the catalyst inner surface (in Fig. 2 they are given separately) were determined in all cases by an extrapolation of the values of the rate constants measured at three lowest catalyst granulations according to the Lagrange interpolation formula[24]. The calculated values of the rate constants k_0 made it possible to determine the effectiveness factor of the catalyst during the measurements. The dependence of this quantity on the catalyst grain size during the experiments in benzene is illustrated in Fig. 3 for three different temperatures. It is obvious that the effectiveness factor of the catalyst decreases with increasing temperature. This fact is brought about by an increase in the Thiele modulus with temperature as the activation energy of a chemical reaction is higher than that of the molecular diffusion. The discussed effect is more pronounced for greater catalyst particles. The influence of temperature on the measured value of the hydrogenation rate constant was studied at all catalyst
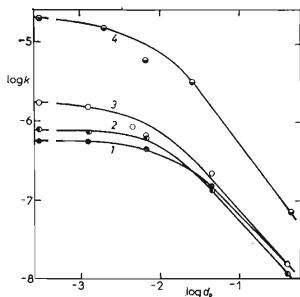

FIG. 2

Dependence of the Hydrogenation Rate Constant in the Solvents Used on the Catalyst Particle Diameter at 25°C

1 Benzene, catalyst I; *2* hexane, catalyst I; *3* methanol, catalyst I; *4* tetrachloromethane, catalyst II.
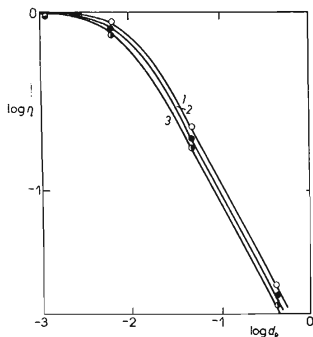
FIG. 3

Influence of the Grain Diameter and Temperature on the Effectiveness Factor of the Catalyst during the Hydrogenation of Cyclohexene in Benzene (Catalyst I)

○ 288 K; ● 298 K; ◖ 308 K.

granulations. The values of the apparent activation energies were determined from the slopes of the Arrhenius curves. The dependence of this quantity on the catalyst grain size is given for all experiments in Fig. 4. The measurements confirmed that the value of the apparent activation energy decreases with an increase in the catalyst particle size approaching a constant value in the region of a strong influence of the internal diffusion. From the values of the apparent activation energies measured at the highest catalyst granulation, the value of the activation energy of the hydrogen diffusion in the solvents was determined with the aid of Eq. (9). The activation energy of the actual reaction in the kinetic region, which is necessary for the calculations, was obtained in the case of the catalyst I (solvents benzene, hexane and methanol) from the measurement at the lowest granulation at which practically a complete utilization of the catalyst inner surface was reached. During the experiments with the catalyst II (solvent tetrachloromethane) the activation energy of the hydrogenation in the kinetic region was again extrapolated by Lagrangian interpolation polynomials from the values of the activation energies measured at three lowest granulations. The resulting values of the activation energy of the hydrogen diffusion in the solvents are summarized in Table II and they are supplemented by the values for similar
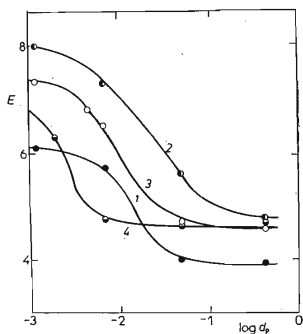

Fig. 4

Dependence of the Apparent Activation Energy on the Catalyst Particle Diameter during the Hydrogenation of Cyclohexene in the Solvents Used

1 Benzene, catalyst I; *2* hexane, catalyst I; *3* methanol, catalyst I; *4* tetrachloromethane, catalyst II.
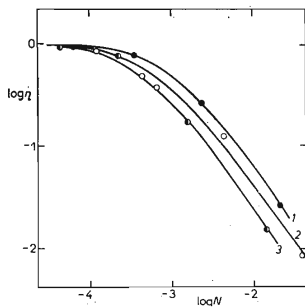
Fig. 5

Solvent Influence on the Dependence of the Effectiveness Factor of the Catalyst I on the Quantity N

● Benzene; ◑ hexane; ○ methanol.

systems, which have been till now published in the literature. In the case hydrogen–tetrachloromethane it is possible to state that our value is in good agreement with the literature data[26]. In spite of this the values measured in this work are on the average lower than the hitherto published activation energies of hydrogen in liquids. This fact is not due to the experimental inaccuracy of the method as the error in the determination of the value of the activation energy of the hydrogen diffusion in a liquid was less than 0.8 kcal mol⁻¹.

From the experimentally determined values of the effectiveness factor of the catalyst it is possible to estimate the tortuosity coefficient of the catalyst. On the assumption that the values of the molecular diffusion coefficient of hydrogen in the solvents are known (for the values employed[8]), the tortuosity coefficient may be established by a combination of Eqs $(2)-(4)$. The calculated values for benzene 1.7, methanol 4.4 and hexane 7.8 differ unexpectedly. This result is also obvious from Fig. 5 illustrating the dependence of the effectiveness factor of the catalyst on the quantity N which is proportional to the Thiele modulus:

$$N = d_p \sqrt{(k_0/D)} . \tag{12}$$

If the tortuosity coefficient assumed the same value in all solvents, the experimental points would have to be approximated by a single curve. It follows unambiguously from the figure that the experimental points for the respective solvents can be approximated only by three different curves. The obtained result can be explained with

TABLE II
Activation Energies (E_D) of the Hydrogen Diffusion in the Liquids (Total Pressure 1 atm)

Solvent	Temperature, K	E_D, kcal mol⁻¹	Lit.
Water	273—298	3·85	25
Tetrachloromethane	273—298	2·6	26
Octadecane	379—473	3·1[a]	27
Cyclohexane	333—373	2·9[b]	28
Cumene	298—343	3·06	2; 3
α-Methylstyrene	298—343	3·21	2; 3
Tetrachloromethane	288—308	2·4	this work
Benzene	288—308	1·7	
Hexane	288—308	1·4	
Methanol	288—308	1·8	

[a] Extrapolated from experimental data measured at higher pressures. [b] Measured at a pressure of 52 atm.

difficulties. The error in the rate constant determination (an average value from several measurements) on the apparatus did not exceed 3 rel.%. The same holds for the rate constant k_0 at a total utilization of the catalyst inner surface. The error of the hydrogen diffusion coefficients in the solvents is approximately[8] $5-6$ rel.%. It is not necessary to consider the inaccuracy in the grain size determination and catalyst porosity as both quantities are identical for the given solvents. It therefore follows from this enumeration that the scatter of the experimental values should not exceed $11-12$ rel.% for all solvents. However, the experimental points in Fig. 5 for the different solvents differ much more from one another (by approximately ± 50 rel.%). The differences in the tortuosity coefficients calculated from the measurements in the respective solvents cannot be explained in any case by the scatter of the experimental points. The established fact might be explained by an assumption that the solvents do not exhibit the properties of inert components but that they influence the catalyst by their adsorption ability; at these conditions it is obviously not possible to take the catalyst porous particle for a pseudohomogeneous medium.

LIST OF SYMBOLS

a	catalyst inner surface related to a catalyst volume unit (cm^{-1})
A_D	frequency factor of the molecular diffusion $(cm^2\ s^{-1})$
A_K	frequency factor of a chemical reaction $(cm\ s^{-1})$
C_H	concentration of hydrogen dissolved in the reaction mixture $(mol\ cm^{-3})$,
C_S	concentration of the substrate $(mol\ cm^{-3})$
d_p	diameter of a catalyst particle (cm)
D	molecular diffusion coefficient $(cm^2\ s^{-1})$
D_{ef}	effective diffusion coefficient $(cm^2\ s^{-1})$
E	apparent activation energy $(kcal\ mol^{-1})$
E_k	activation energy of a chemical reaction $(kcal\ mol^{-1})$
E_D	activation energy of the molecular diffusion $(kcal\ mol^{-1})$
ΔH	differential heat of solution of hydrogen in the liquid phase $(kcal\ mol^{-1})$
k	rate constant of a reaction $(cm\ s^{-1})$
k_0	reaction rate constant at a total utilization of the catalyst inner surface $(cm\ s^{-1})$
N	parameter (Eq. (12)) $(cm^{1/2})$
P_b	atmospheric pressure (Torr)
P^0	saturated vapour pressure of the liquid phase (Torr)
Q	Thiele modulus
r_0	initial reaction rate $(mol\ s^{-1}\ cm^{-2})$
R	gas constant $(kcal\ mol^{-1}\ grad^{-1})$
T	absolute temperature (grad)
y	parameter (Eq. (1))
η	effectiveness factor of the catalyst
Θ	catalyst porosity
τ	tortuosity coefficient of the catalyst
ψ	parameter (Eq. (7))

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Translated by K. Hlavatý.