INTERNAL DIFFUSION EFFECT AND HYDROGENATION SELECTIVITY OF 1,5-CYCLOOCTADIENE

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A relatively selective hydrogenation of 1,5-cyclooctadiene to cyclooctene has been achieved in cyclooctane solution at atmospheric pressure using a powder catalyst with 0.6% (by wt.) palladium on γ-alumina. The cyclooctene yields are temperature independent within 30 to 50°C, they are, however, markedly decreased with the use of the tablet catalyst.

Selective hydrogenation of 1,5-cyclooctadiene to cyclooctene in liquid phase represents a procedure enabling preparation of a relatively reactive intermediate with auspicious importance for organic synthesis. One of potential uses of cyclooctene is its oxidation to suberic acid[1] which can be used for synthesis of special oils, plasticizers, polyesters, polyamides *etc.* So far selective hydrogenation of 1,5-cyclooctadiene to cyclooctene has been dealt with predominantly in patent literature[2,3]. The main aim of this work is to show the influence of reaction temperature and diffusion transfer of the reaction components in the catalyst grain on selectivity of the studied reaction. The obtained knowledge can be used also for analogous hydrogenation processes, *e.g.* selective hydrogenation of fats.

The hydrogenation kinetics of 1,5-cyclooctadiene was studied in our previous works[4,5]. In ref.[4] a kinetic model is suggested for this hydrogenation presuming the first orders of the consecutive reactions with respect to concentration of the olefins. The hydrogenation was studied in methanolic medium with palladium catalyst Pd/γ-Al$_2$O$_3$. If, however, cyclooctane and palladium on charcoal were used as the solvent and the catalyst, respectively, it was found[5] that the presumption of the first order of the individual reactions was not fulfilled, and the reaction system must be described by a more complex kinetic equation with the use of the Langmuir–Hinschelwood equations. Hence the kinetic parameters depend on the catalyst used and the reaction medium.

An analogous system was studied in a recent paper[6]. Stepwise hydrogenation of methyl linoleate through methyl oleate to methyl stearate was carried out in liquid phase in a discontinuous reactor using palladium catalyst of various dispersity, and it was found that influence of internal diffusion on kinetics and selectivity of the consecutive reactions presents a complex problem. In the paper cited a procedure for evaluation of experimental data is also suggested.

A part of catalyst is inefficient, if the inner mass transfer is significantly imperfect. This influence is characterized by the effectiveness factor of the catalyst[12]:

$$E = r/r_{kin} . \qquad (1)$$

The kinetic-region reaction rate r_{kin} must be determined with the catalyst of sufficiently small grain, whereas the reaction rate r is affected by the diffusion mass transfer inside a greater catalyst grain. Influence of internal diffusion on the hydrogenation course of olefins in liquid phase was followed e.g. in refs[7−9].

Selectivity of the consecutive reactions depends considerably on utilization of the inner surface of the catalyst grain[10,11]. The effect of imperfect mass transfer in catalyst grain reduces the selectivity of consecutive reactions, because inside the catalyst grain there is a lower concentration of the starting substance and a higher concentration of the intermediate than at the catalyst surface, which favours the second reactions. Hence, in kinetic region the reaction selectivity is maximum, and it decreases with decreasing E factor (in the middle region, i.e. $1 > E > 0.3$), being ultimately close to the value corresponding to strong effect of internal diffusion[12] (for $E < 0.3$).

EXPERIMENTAL

Reagents

1,5-Cyclooctadiene was prepared[13] by selective cyclodimerization of 1,3-butadiene in an apparatus of the plant Kaučuk, Kralupy n/Vlt. using a homogeneous complex nickel catalyst; the raw product was rectified on a laboratory column having 20 TP (b. p. 149°C/0·1 MPa).

Cyclooctene was prepared by selective hydrogenation of 1,5-cyclooctadiene in a 2·5 l autoclave at 70°C and 1—2 MPa hydrogen pressure using the below-given catalyst; the reaction mixture containing 30% (by wt.) cyclooctane was used for further experiments without purification.

Cyclooctane was prepared by hydrogenation of 1,5-cyclooctadiene in the same autoclave at 150°C and 5 MPa hydrogen pressure using a catalyst with 3% (by wt.) palladium on charcoal (b. p. 150°C/0·1 MPa).

Hydrogen was commercial, electrolytical, quality B (Technoplyn, Prague).

The catalyst contained 0·6% (by wt.) palladium on γ-alumina (Chemické závody, Litvínov); for the experiments it was used in the form of equilateral cylinders 4 . 4 mm, a part of the catalyst was quartered to 2 . 2 mm grain and further ground to powder; from this powder a fraction of the grain size below 0·05 mm was obtained by sieving and used for the measurements in kinetic region. Distribution of palladium in the catalyst tablets was not uniform, the metal being present in a surface layer thinner than 0·2 mm.

Apparatus and Procedures

All the experiments were carried out in glass reactors under atmospheric pressure at 30 to 50°C in cyclooctane solutions. The hydrogenations using the powder catalyst were carried out in the standard apparatus[14], the hydrogenation kinetics with the tablet catalyst was measured in the

reactor described elsewhere[15]. The experiments were carried out with stirring intensive enough to prevent the effects of external diffusion of the reactants on the reaction rate, *i. e.* 800 swings per min or 1 200 rpm. The tablet catalyst was placed in the reactor in a wire gauze basket forming the stirrer. The basket capacity was either 0·62 g catalyst tablets 4 . 4 mm or 0·85 g quartered catalyst 2 . 2 mm grain. The solutions to be hydrogenated contained 1—5% (by wt.) olefin in cyclooctane. At regular time intervals samples were withdrawn from the reaction mixture for chromatographical analysis.

Analysis

The samples of the reaction mixture were analyzed on a gas chromatograph Chrom-2 with flame-ionization detection. The components were separated in a 9 m . 2·5 mm column packed with 15% polyethylene glycol 6000 on Chromaton N-AW, size 0·2—0.5 mm. Temperature 76°C; nitrogen flow rate 0·025 ml/s; air flow rate 0·167 ml/s; hydrogen pressure 26·7 kPa; feed 0·5 μl; sensitivity 1 : 100. Relative elution times: cyclooctane 1; cyclooctene 1·1; 1,3-cyclooctadiene 1·5; 1,5-cyclooctadiene 1·9. The amounts of cyclooctene and 1,5-cyclooctadiene were determined with the use of planimeter and calibration graphs. The 1,3-cyclooctadiene content in the samples of the reaction mixture was negligible, and, therefore, isomerization was presumed not to take place.

Evaluation of Kinetic Measurements

Initial hydrogenation rates of the olefins were determined from the slopes of time dependences of their concentration at the start of the reaction. Presuming the reaction order to be unity with respect to hydrogen, we introduced a correction of the measured reaction rate r with respect to changes of the barometric pressure P_{bar} (Eq.(*1*)), where P^0 is the cyclooctane vapour pressure

$$r_{corr} = 1·0133 . 10^5 \, r/(P_{bar} - P^0) \qquad (2)$$

at the temperature of the measurement. The hydrogenation activation energy was determined from the Arrhenius relation of the reaction rate vs temperature. The reaction rate values were measured with an error less than 10% rel.

RESULTS AND DISCUSSION

The hydrogenation course of 1,5-cyclooctadiene. Typical time dependences of the reaction mixture composition measured during hydrogenation of 1,5-cyclooctadiene are presented in Figs 1—4. Figs 1 and 2 relate to kinetic region at 30 and 50°C, respectively, Figs 3 and 4 relate to the experiments carried out at 40 and 30°C, respectively, in which the reaction was affected by diffusion of the reaction components in the catalyst particles 2 mm and 4 mm, respectively. The experimental results indicate in all the cases that the rate of formation of cyclooctane is not equal to zero at the beginning of the reaction. This fact is connected with the initial rate of formation of cyclooctene being somewhat lower than that of consumption of 1,5-cyclooctadiene.

Obviously the obtained data cannot be described by a simple kinetic scheme of two consecutive hydrogenation steps. For elucidation of the found data it seems reasonable to presume (as it was the case with hydrogenation of methyl linoleate[6]) the
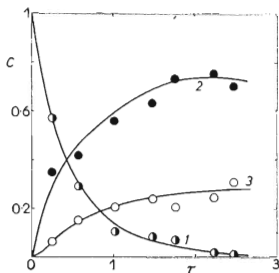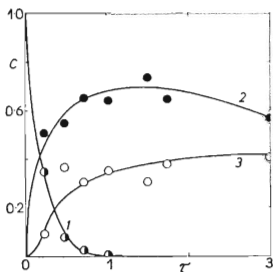
FIG. 1

Time-Composition Dependence of Reaction Mixture during Hydrogenation of 1,5-Cyclo-octadiene in Kinetic Region

$t = 30°C$, $c_o = 0.285$ kmol/m^3, $d_p < 0.05$ mm; *1* 1,5-cyclooctadiene, *2* cyclooctene, *3* cyclooctane.

FIG. 2

Time-Composition Dependence of Reaction Mixture during Hydrogenation of 1,5-Cyclo-octadiene in Kinetic Region

$t = 50°C$, $c_o = 0.285$ kmol/m^3, $d_p < 0.05$ mm; for numbers see Fig. 1.
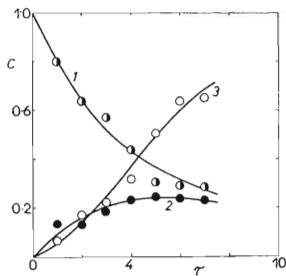

FIG. 3

Time-Composition Dependence of Reaction Mixture during Hydrogenation of 1,5-Cyclo-octadiene in Diffusion Region

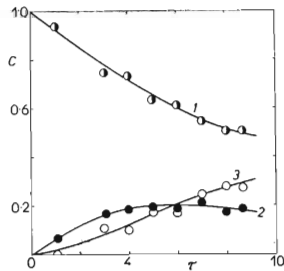$t = 40°C$, $c_o = 0.285$ kmol/m^3, $d_p = 2$ mm; for numbers see Fig. 1.

FIG. 4

Time-Composition Dependence of Reaction Mixture during Hydrogenation of 1,5-Cyclo-octadiene in Diffusion Region with Tablet Catalyst

$t = 30°C$, $c_o = 0.285$ kmol/m^3, $d_p = 4$ mm; for numbers see Fig. 1.

existence of a non-equilibrium adsorption of the reaction components at the catalyst surface during the hydrogenation. With this presumption the hydrogenation of 1,5--cyclooctadiene can be simplified to the following reaction system:
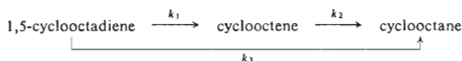
$$1,5\text{-cyclooctadiene} \xrightarrow{k_1} \text{cyclooctene} \xrightarrow{k_2} \text{cyclooctane}$$

with k_3 connecting 1,5-cyclooctadiene to cyclooctane.

TABLE I

Influence of Catalyst Grain Size on the Hydrogenation Rate and the Maximum Cyclooctene Concentrations

$t = 30°C$; $c_0 = 0.285$ kmol m^{-3}.

Grain size d_p, mm	Initial rate r_0, kmol m^{-3} s^{-1} g^{-1}		Max. concentration of cyclooctene C (% by wt.)
	COD	CEN	
<0.05	$1.33 \cdot 10^{-3}$	$2.11 \cdot 10^{-5}$	75
2	$1.61 \cdot 10^{-5}$	$4.01 \cdot 10^{-6a}$	23
4	$1.04 \cdot 10^{-5}$	—	20

[a] $t = 40°C$.

TABLE II

Effectiveness Factors of Catalyst in Hydrogenation of 1,5-Cyclooctadiene and Cyclooctene

Grain size d_p, mm	Temperature t, °C	Effectiveness factor of catalyst E	
		COD	CEN
4	30	0.008	—
2	30	0.012	0.085
2	40	0.008	0.067
2	50	0.005	0.062
<0.05	30—50	1^a	1^a

[a] Presumption.

Influence of size of catalyst particles. The time-concentration dependences at the beginning of hydrogenations of both 1,5-cyclooctadiene and cyclooctene were used for determination of the initial reaction rates which are given in Table I along with the maximum cyclooctene concentration reached in hydrogenation of 1,5--cyclooctadiene (with various catalyst grain sizes).

From these data it is obvious that the retarding effect of the diffusion transfer of the reaction components in porous structure of the catalyst grain results not only in the expected marked lowering of the reaction rates but also in a considerable selectivity decrease of the hydrogenation of 1,5-cyclooctadiene to cyclooctene, which is indicated by substantially lower maximum cyclooctene concentration in the reaction mixture. Effect of the inner diffusion on the hydrogenation course is also clear in Figs 1, 3 and 4 relating to the catalysts of the given grain size.
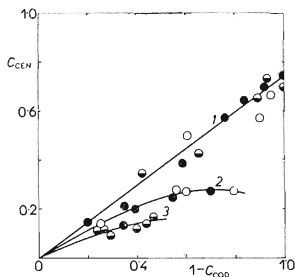
TABLE III

Activation Energies (kJ/mol) of Hydrogenation of 1,5-Cyclooctadiene and Cyclooctene in the Kinetic and the Diffusion Regions

Region	COD	CEN
Kinetic	50	52
Diffusion	13	16

FIG. 5

Influence of Temperature and Catalyst Grain Size on Selectivity of Hydrogenation of 1,5--Cyclooctadiene

Temperature 30°C (◓), 40°C (●), 50°C (○); *1* $d_p < 0.05$ mm, *2* $d_p = 2$ mm, *3* $d_p = 4$ mm.

The catalyst used contained palladium impregnated in an only very thin surface layer of the used carrier. In spite of that, the measured values of the initial reaction rates were used for calculation of the apparent effectiveness factor of the catalyst tablets (E) (see Eq. (*1*) with the presumption of full utilization of the surface of the powder catalyst). From the results in Table II it follows that the hydrogenation of both 1,5-cyclooctadiene and cyclooctene proceeded (with the use of the tablet catalyst at all the temperatures investigated) in the region of strong internal diffusion effect, *i.e.* $E < 0.3$.

In accordance with theory, the effectiveness factor of the catalyst is inversely proportional to the catalyst grain size, and it decreases with increasing temperature. The results in Table II also indicate that the catalyst is better utilized in the hydrogenation of cyclooctene; this reaction being slower, the concentration gradients formed inside the catalyst grain are better compensated by diffusion.

Effect of temperature. Comparison of Figs 1 and 2 (kinetic region, temperatures 30 and 50°C, respectively) shows that the maximum cyclooctene yield is practically independent of the hydrogenation temperature. This fact is also confirmed by the found values of the activation energies, determined from the initial hydrogenation rates of 1,5-cyclooctadiene and cyclooctene, which are compared with the activation energies found in the diffusion region (Table III).

The values corresponding to the diffusion region are low (in accordance with theory), they are, however, smaller than half the value of the activation energy found in the kinetic region. This fact can probably be explained by experimental error in determination of the reaction rates.

Dependence of cyclooctene concentration on the conversion of 1,5-cyclooctadiene hydrogenation measured at various temperatures and with catalysts of various grain size are summarized in Fig. 5. This figure documents the fact that influence of temperature on the hydrogenation course is slight in both the kinetic and the diffusion regions.

LIST OF SYMBOLS

c	concentration [kmol m^{-3}]
$C = C/C_0$	relative concentration [—]
d_p	catalyst grain diameter [mm]
E	effectiveness factor of catalyst [—]
P^0	vapour pressure of reaction mixture [Pa]
P_{bar}	barometric pressure [Pa]
r	reaction rate [kmol m^{-3} s^{-1} g$_{cat}$$^{-1}$]
t	temperature [°C]
τ	time [h]
COD	1,5-cyclooctadiene
CEN	cyclooctene

Indexes

o   the initial value
diff   the value in the diffusion region
kin   the value in the kinetic region
corr   the corrected value

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