EFFECT OF INTERNAL DIFFUSION ON KINETICS OF LIQUID PHASE HYDROGENATION AND DISPROPORTIONATION OF CYCLOHEXENE ON PALLADIUM CATALYSTS

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Dedicated to late Academician Eduard Hála.

Kinetics of the side reactions represented by the system involving hydrogenation and disproportionation of cyclohexene on a commercial catalyst CHEROX 41-00 (3% Pd/C) and on a supported palladium catalyst prepared by impregnation of alumina with aqueous palladium dichloride (2·15% Pd/γ-Al$_2$O$_3$) have been investigated. As follows from the effectiveness factors of internal diffusion for individual reactions, in the region of internal diffusion, cyclohexene hydrogenation is preferred compared to disproportionation. This finding can be related to the fact that while the rate of disproportionation is controlled by cyclohexene diffusion, the rate of hydrogenation is controlled by diffusion of hydrogen.

In the present work we report on the measurements of the activity of palladium catalysts for hydrogenation (r_H) and disproportionation (r_D) of cyclohexene in cyclohexane as a solvent. The above system of side reactions is depicted in the following scheme.
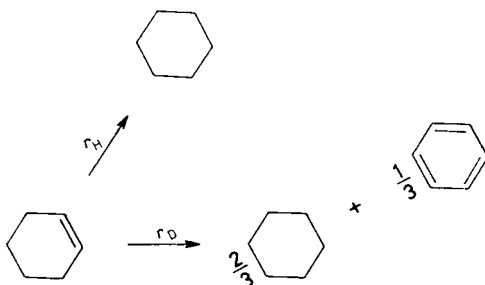
SCHEME 1

This reaction system was used in our several previous studies[1-3] on the behaviour of trickle-bed reactors. We observed that disproportionation reaction is preferred at overheating the catalyst in hot regions of the catalyst bed. Therefore, the aim of the present study was to elucidate kinetics of the two reactions, and that in the kinetic region as well as in the regime with the strong effect of internal diffusion. We were also interested in the effect of radial activity profile on the course of side reactions, as according to theoretical prediction[4,12], a catalyst containing an active component centered at external particle surface is the more advantageous.

The effectiveness factor of internal diffusion η was defined in the usual way[4] as the quotient of the reaction rate in diffusion regime r and the reaction rate r_k determined at excluding the effect of internal diffusion under otherwise identical conditions:

$$\eta = r/r_k .$$ (1)

EXPERIMENTAL

Chemicals and Catalysts

Hydrogen (electrolytic, Technoplyn Prague), cyclohexane (pure, Lachema Brno), cyclohexene (prepared by dehydration of cyclohexanol with sulfuric acid[5] and rectified after drying on 20 TP column, b.p. 82°C), cyclohexanol (pure, Lachema Brno), sulfuric acid (analytical purity, Lachema Brno), palladium(II) chloride (analytical purity, Safina Vestec), γ-alumina (Pural SB, Condea (F.R.G.), extrudates having diameter 1·8 mm and medium length 7 mm). Catalyst CHEROX 41-00 (3% Pd/charcoal; produced by Chemopetrol CHZ ČSSP Litvínov) was used as extrudates with 3·4 mm diameter and 5 mm medium length.

Catalyst K II was prepared by impregnation of 15 g of the extrudates of γ-alumina with aqueous palladium(II) chloride (3·3 g/400 ml) in the apparatus described earlier[6] (at 25°C for 4 h). The catalyst containing 2·15 mass % Pd was reduced with stoichiometric amount of formaldehyde (3·6 ml of formaldehyde in 400 ml of distilled water) and then dried at 60°C/4 kPa for 2 h. The portion of the extrudates of both catalysts was disintegrated after reduction and sieved through a sieve with 0·04 mm apertures.

Palladium Distribution in Catalyst Particles

Profiles of palladium distribution in catalyst extrudates were measured by electron microanalysis[7], using the scanning electron microscope JEOL JSM 50-A combined with the energy dispersion X-ray analyzer EDAX-711. The obtained dependence of the intensity of X-ray irradiation, corresponding to L_α line of palladium, on the radial coordinate of catalyst particle was transformed into concentration dependence. Radial concentration profiles for the catalysts used are shown in Fig. 1. They demonstrate that CHEROX 41-00 catalyst contains the majority of the metal at the extrudate surface while the catalyst K II has palladium centered more within the particle. The procedure employed in the preparation of this catalyst yielded the optimal profile with regard to the abrasion and palladium losses on manipulation with the catalyst (surface core of the extrudates contained palladium in very low concentration).

Apparatus and Procedure

Measurements with catalyst powder were performed in the apparatus described in detail in earlier work[8]. The apparatus consisted of a glass isothermic isobaric reactor, the intense stirring of which was ensured by a magnetic stirrer. The reactor was connected to a set of temperature--controlled gas burettes closed with a liquid and filled with hydrogen.

Reactions were carried out at 30°C and at atmospheric pressure in the kinetic region with respect to the internal and external diffusion. The effect of internal diffusion was eliminated by a sufficiently small granulation of the catalyst (0·04 mm). Hydrogenation was followed by the decrease in hydrogen volume in the gas burette. Kinetics of both reactions was measured based on changes in the composition of reaction mixture; during experiments, samples of the reaction mixture were withdrawn from the reactor and analysed chromatographically.

The study of the reactions with catalyst in the form of extrudates was made in the apparatus[9] which consisted of a glass isothermic 100 ml-reactor placed in a temperature-controlled bath. The catalyst was placed into a wire basket in the shape of stirrer blades and the whole reaction system was stirred with this basket. This arrangement eliminated gradual abrasion or disintegration of the catalyst during the reaction.

The reactor proper was provided with 4 vertical baffles which prevented formation of a centre vortex in the liquid; hydrogen was introduced below the stirrer after previous saturation with vapours of the liquid phase. In experiments the rates of formation of cyclohexane (produced by hydrogenation and simultaneous disproportionation) and of benzene formation were examined. These data were used to calculate the rates of hydrogenation of cyclohexene to give cyclohexane and the disproportionation of cyclohexene, yielding cyclohexane and benzene. The ratio of the reaction rates on the disintegrated and nondisintegrated catalyst were used to determine the effectiveness factor of the catalyst.

Analytical Method

Samples of reaction mixtures were analysed gas chromatographically — 2·5 m long column, 15% poly(ethylene glycol) on Chromosorb NAW-DMSC, 70°C, flame-ionisation detector, nitrogen flow rate 10 ml/l. The following relative elution times were obtained: cyclohexane 1·0, cyclohexene 1·48, benzene 3·1. The accuracy of determination amounted to c. 3 rel. per cent.
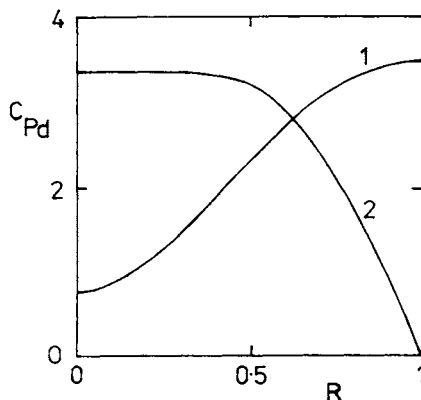

FIG. 1

Radial palladium distribution in catalyst particle. 1 CHEROX 41-00, 2 catalyst K II

RESULTS AND DISCUSSION

Kinetics of Hydrogenation and Disproportionation of Cyclohexene

Kinetics of both reactions were measured in the liquid phase (cyclohexane as the solvent) with powdered catalyst at 30°C and at atmospheric pressure in the kinetic region with respect to the internal and external diffusion. To determine reaction orders in cyclohexene, a series of experiments with different initial concentrations of the substrate was carried out. Dependencies of the initial reaction rates of hydrogenation and disproportionation on the initial substrate concentration are represented graphically in logarithmic coordinates in Fig. 2. The results show that the catalyst K II exhibits the enhanced activity compared to the commercial sample and that both for the hydrogenation (c. five times) and disproportionation (c. twice) of cyclohexene (see also Table II). Reaction orders determined from the slopes of linear dependences are presented in Table I. It is of interest that while with commercial catalyst CHEROX 41-00 the reaction orders for both reactions are close to zero, the reaction orders found for the catalyst prepared in our laboratory are different. The order of hydrogenation was close to one while the order of disproportionation reaction was low (approximately zero).

The Effect of Internal Diffusion

Further study was centered to measurements of the activity of nondisintegrated particles of both catalysts. The effect of external diffusion was supressed by sufficient frequency of revolutions of the stirrer containing the catalyst. Initial reaction rates of both reactions are compared in Table II with the results obtained in the kinetic region with respect to internal diffusion.
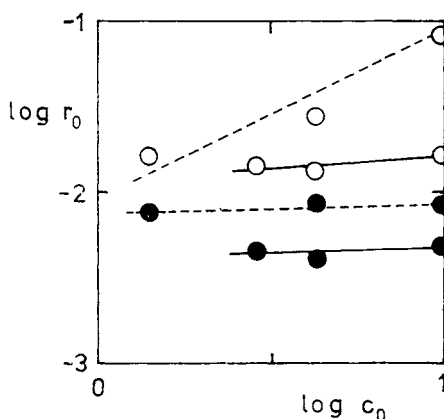

FIG. 2

Determination of reaction orders of hydrogenation (○) and disproportionation (●) of cyclohexene for catalysts CHEROX 41-00 (solid line) and K II (broken line)

The results demonstrate that the measurement with nondisintegrated catalysts was performed under strong effect of internal diffusion of reaction components in catalyst particles. As particles of the commerical catalyst are markedly greater the reaction rates obtained for catalyst CHEROX 41-00 were significantly lower than those determined for catalyst K II.

The reaction rates for powdered and nondisintegrated catalysts were used to calculate effectiveness factors of internal diffusion assuming that the utilization of internal surface is complete in the case of powdered catalysts (Table II). Although catalyst CHEROX 41-00 is the less active for the reaction system used than the catalyst K II, the effectiveness factors of internal diffusion acquire lower values. This can be accounted for by that we deal here above all with the effect of particle size, as the catalyst CHEROX 41-00 has particle diameter 2·5-times greater compared

TABLE I
Reaction orders of hydrogenation and disproportionation of cyclohexene in kinetic region

Catalyst	Reaction order	
	hydrogenation	disproportionation
CHEROX 41-00	0·2	0·07
K II	1·1	0·06

TABLE II
Initial reaction rates r (mol/kg h) and effectiveness factors of internal diffusion η (%) for hydrogenation and disproportionation of cyclohexene ($C_0 = 9\cdot9$ mol l^{-1})

Catalyst	d_{cat}, mm[a]	Hydrogenation		Disproportionation	
		r_H	η_H	r_D	η_D
CHEROX 41-00	0·04	16	100	4·6	100
	(1·51)	—	(4·2)	—	(1·5)
	3·42	0·31	1·9	0·033	0·7
K II	0·04	84	100	8·7	100
	1·51	2·9	3·5	0·16	1·8

[a] Mean diameter of catalyst particle.

to the K II catalyst. As follows from comparison of the effectiveness factors of internal diffusion for single reactions, for hydrogenation they are higher for both catalysts than those for disproportionation, since the rate of cyclohexene disproportionation in the kinetic region is lower. This finding relates to the fact that in the region of internal diffusion, the rate of hydrogenation is limited by diffusion of hydrogen (the concentration of which in liquid phase is markedly lower than that of the other reaction component-cyclohexene), while the rate of disproportionation is controlled evidently by diffusion of cyclohexene which, when compared to hydrogen, has significantly greater molecule and thus also lower diffusion coefficient. The values of molecular diffusion coefficient of hydrogen in cyclohexane[10] and of self-diffusion coefficient of cyclohexane[11] are $1.73 . 10^{-8}$ and $1.88 . 10^{-9}$ m^2/s, respectively (diffusion coefficient for cyclohexene is not available). Providing that molecules of cyclohexane and cyclohexene are of the same size, the rate of diffusion of hydrogen in the reaction mixture is then by one order of magnitude faster than that of cyclohexene diffusion. For purposes of comparison, in Table II are presented also in parentheses the effectiveness factors of internal diffusion calculated utilizing the inverse proportion of the effectiveness factor on the catalyst particle size in the region of the strong effect of internal diffusion. It is worth mentioning that while for hydrogenation, the factor for the less active catalyst CHEROX 41-00 is higher (as follows from theory of internal diffusion), in the case of disproportionation both values are comparable to each other. This discrepancy cannot be accounted for by a non-uniform distribution of the active component in catalyst particles (cf. Fig. 1), which according to theory[12] is more suitable for the commercial catalyst. As due to its low concentration, hydrogen is the key component in the reaction mixture, it seems likely that disproportionation of cyclohexene occurs only when a sufficient amount of hydrogen is adsorbed at the internal catalyst surface. Therefore, also the selectivity of hydrogenation (see later) is higher in the diffusion region and on using the more active catalyst.

TABLE III

Selectivity of hydrogenation of cyclohexene in kinetic and diffusion region

Catalyst	Selectivity	
	kinetic region	diffusion region
CHEROX 41-00	0·78	0·90
K II	0·91	0·95

Selectivity of Hydrogenation in Kinetic and Diffusion Regions

Study of kinetics of hydrogenation and disproportionation of cyclohexene in kinetic and diffusion region made it possible to determine selectivity of the reaction system with respect to hydrogenation, defined as the ratio of hydrogenation rate r_H to the total rate of substrate consumption, i.e. by the relation

$$ S = \frac{r_H}{\left(r_H + r_D \right)} , \tag{2} $$

where r_D denotes the disproportionation reaction rate.

The obtained selectivities for kinetic and diffusion regime are presented in Table III. The results demonstrate that on going from kinetic to diffusion region, hydrogenation becomes preffered on both catalysts. The higher selectivity of cyclohexene hydrogenation in diffusion region can be related to the fact that diffusion transport of hydrogen (which is the key component of hydrogenation) is faster than diffusion transport of cyclohexene in catalyst particles.

LIST OF SYMBOLS

c	concentration of cyclohexene, $kmol/m^3$
C_{Pd}	palladium concentration in catalyst, mass %
r	reaction rate, $mol/kg\ h$
R	dimensionless radial coordinate of particle, — ($R = 0$ center, $R = 1$ border)
S	selectivity, —
η	factor of internal diffusion effectiveness, %

Subscripts

D	disproportionation
H	hydrogenation
k	kinetic region
0	initial value

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