HYDROGENATION OF NITROBENZENE ON PALLADIUM IN A NEW TYPE OF TRICKLE-BED REACTOR

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A study of the hydrogenation kinetics of nitrobenzene on a palladium catalyst deposited on vertical sheets of expanded metal has confirmed that this new type of the reactor packing for reactions proceeding in the liquid phase is advantageous from the point of view of the transfer of hydrogen to the catalyst surface. This is brought about by a large contact surface of the liquid and gaseous phases, by the mixing of the liquid trickling the catalyst surface and by a good accessibility of the catalyst surface. On the contrary, easy poisoning by impurities in the feed was observed which is due to a lower specific surface of the active metal in comparison with catalysts prepared by depositing the metal on high surface area carriers.

Existing studies on flow reactors for three-phase liquid–gas–solid catalyst systems have been aimed at two directions. On the one hand, it is a practically oriented research on trickle-bed reactors with pellet catalysts, on the other hand they are studies of simple model reactions between a liquid and a gas on a compact metal or metallized wall which makes it possible to verify the theoretical model of three-phase systems.

The aim of this work was a kinetic measurement of the reaction between a gas and a liquid flowing down on a solid catalyst deposited on the surface of a carrier made of an expanded metal. Vertical expanded metal sheets were proved to be an excellent packing for absorption columns with high efficiency and low hydrodynamic resistance[1-5]. In an effort to exploit the ability of expanded metal to assure good conditions for contact of liquid and gas also in the case of absorption followed by a catalyzed chemical reaction, methods were developed for preparing different types of catalyst surfaces carried on expanded metal[6,7]. The study of kinetics on this catalyst should indicate conditions at which the transfer of the gas through the liquid film to the catalyst surface would not diminish the rate of the total process. The hydrogenation of nitrobenzene on metallic palladium yielding aniline was chosen as the model reaction:

$$C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O. \qquad (A)$$

This reaction proceeds sufficiently rapidly, so that experiments at normal pressure and mild temperatures were possible. The enthalpy of reaction (A) is (ref.[8]) $\Delta H = -106\cdot6$ kcal/mol at 293 K.

EXPERIMENTAL

Materials used. n-Butanol, pure (Lachema, Brno) was freshly distilled before use, b.p. 118°C; nitrobenzene, AR grade (Lachema, Brno) was distilled in vacuum, b.p. 102°C/12 Torr; palladium chloride was delivered as a 10% solution (Kovohutě, Vestec).

Catalyst. The catalyst carrier was formed by expanded aluminium plates with openings of the size of 10 × 5 mm. The structure of the expanded metal is depicted schematically on Fig. 1. This carrier was metallized by the following method: the surface of degreased expanded metal strips was activated in a 10% solution of NaOH for approximately 2 min. After rinsing in water, the strips were submerged into a 1% aqueous solution of palladium dichloride. The reduction led to the formation of an uniform layer of metallic palladium on the catalyst surface. The solution was agitated during the reduction. The catalyst was dried and activated in a reactor in a stream of pure hydrogen for two hours at 60°C. The resulting thickness of the palladium layer, which is in a relation to the degree of dispersion of the catalyst, was controlled by the concentration of the solution of palladium chloride and the reaction time. This preparation yielded a catalyst of reproducible activity (reaction rates on catalyst packings prepared in the same way differed approximately within other experimental errors, *i.e.* ±10 relative %). The specific surface of the catalyst employed as a reactor packing during the kinetic measurements was determined by adsorption of oxygen in an apparatus described in another work[9] from our Institute and the calculation of the specific surface of the metal was performed according to Bujanova, Ibragimova and Karnauchov[10]. The resulting value of the specific surface related to one gram of palladium is 17 m²/g and the dispersion of the metal expressed as the ratio of the surfacial to the total number of palladium atoms is 0·035. The error in these data amounts approximately to ±20 relative %. It follows from a comparison with published values of specific palladium surfaces that the surface of Pd on the expanded metal is approximately twice as large as the surface of powdered
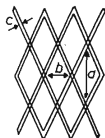

Fig. 1
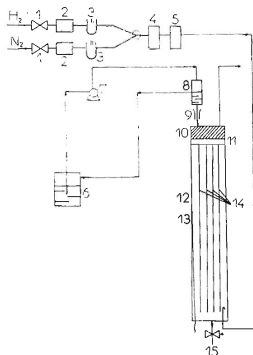
Scheme of Expanded Metal Geometry
a 10 mm, *b* 5 mm, *c* 1 mm.

FIG. 2

Scheme of the Apparatus
For the the description *cf.* text.

palladium black prepared by the reduction of $PdCl_2$ by a $NaBH_4$ solution[11] and ten times smaller than the palladium surface on a carrier catalyst (3—10% Pd on γ-alumina)[10].

Flow apparatus (Fig. 2). Vertical expanded metal strips with the catalyst surface were trickled by the liquid in the flow reactor in a countercurrent arrangement. The liquid wetted only the packing made of the expanded metal. The gases (hydrogen and nitrogen) were led through reduction gages **1**, manostats **2** and flow-meters **3** into purifying columns **4** and **5**. Column **5** contained a Pd/kieselguhr catalyst serving for removal of trace amounts of oxygen. The gases were dried on a molecular sieve in column **5** and led to the reactor bottom. The liquid n-butanol solution of nitrobenzene was pumped from reservoir **6** by a circulation pump **7** into vessel **8**. A constant height of the liquid column over the reactor was maintained by overflow in vessel **8**. The flow of the liquid was controlled by an exchangeable capillary **9**. Column **10** contained crushed glass serving for the distribution of the liquid over the whole crosssection of the apparatus and for a partial saturation of the liquid by the gas. The distributor head **11** was formed by a teflon plug of the diameter of 3·5 cm with four parallel openings into which the expanded metal strips were inserted. The width of a single strip was 2 cm and the total length carrying the catalyst was equal to 60·5 cm. The total packing of the reactor had consequently an area of $4 \times 2 \times 60.5 = 484$ cm^2 and it contained 0·14 g of palladium. Liquid samples were taken from stop-cock **15**. A constant temperature was maintained in reactor **12** and it was controlled by thermocouple **13** registering the temperature of the flowing gas. The entering part of the reactor packing was not coated by the catalyst. This uncoated part was approximately 4 cm long and it served for saturating the liquid by the gas and for preheating the liquid to the reaction temperature. Samples of the liquid were analyzed by gas chromatography. The initial activity of the catalyst decreased approximately to one-twentieth after 2—3 min. The further decrease of the activity was negligible and the activity became constant approximately 5 min from the beginning of the experiment. The time of stabilization of the activity was affected by the flow rate of the liquid; it decreased with increasing flow rate of the liquid. Before each experiment, the catalyst had been regenerated in flowing hydrogen for two hours at 60°C and it assumed the original activity. The partial pressure of hydrogen was being diminished by dilution with nitrogen. A total volume rate of the gas of 1 500 cm^3/min was used during all experiments due to the established fact that this flow rate of gas secured a high molar excess of hydrogen with respect to the liquid substrate and that it ex-
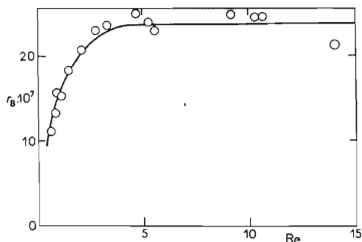

Fig. 3

Dependence of the Reaction Rate on the Reynolds Number
$p(H_2) = 1$ atm, temperature 60°C.

cluded the lowering in the partial pressure of the reacting gas resulting from the transfer of hydrogen through the diffusional film at the surface of the liquid. The hydrogenation of nitrobenzene in the liquid phase is of the zeroth order with respect to nitrobenzene, as it has been verified later on. The rate of decrease in the nitrobenzene concentration could be consequently calculated from the relation:

$$-r_{\mathrm{B}} = \Delta x_{\mathrm{B}} F_{\mathrm{B}}^0 / W \,. \tag{1}$$

The reaction rate in Eq. (1) is related to the unit area of the reactor packing coated by the catalyst.

Static apparatus. Kinetic data, which were independent of the experiments performed in the flow apparatus, were obtained in a batch arrangement. The apparatus consisted of a vibrator with a flask connected through a gas burette to a source of hydrogen. A teflon head with three openings for the expanded metal strips coated by the catalyst was fastened in the ground glass joint of the flask. This arrangement made it possible for the catalyst packing to be fixed in the flask axis, so that no separation of palladium from the expanded metal occurred during the experiments. The liquid was being mixed with hydrogen and it rinsed the catalyst. The reaction rate in the static apparatus was calculated from the relation:

$$-r_{\mathrm{B}} = \Delta x_{\mathrm{B}} C_{\mathrm{B}}^0 V / \tau W \,. \tag{2}$$

Analysis. The conversion of nitrobenzene to aniline was determined analytically on a Chrom 2 gas chromatograph with the flame-ionization detector. The column was 2 m long with its inner diameter of 4 mm, packed with 3% OV 17 (methylphenylsiloxane) on Chromosorb G DMCS 80/100. The temperature in the column was 150°C, the flow rate of nitrogen 20ml/min and the amount of the sample 1 μl.

RESULTS AND DISCUSSION

Character of the flow. The resistance of the trickling liquid layer against the transfer of the gas towards the catalyst surface affects decisively the reaction rate in a gas–liquid–solid catalyst system in a flow apparatus. The lower the density of wetting of the catalyst by the liquid, the more is the reaction retarded by the low hydrogen transfer rate in the liquid. The dependence of the reaction rate on the Reynolds criterion as determined for the reaction between a 5% n-butanol solution of nitrobenzene and hydrogen at 60°C is depicted in Fig. 3. The Reynolds criterion has been defined by the relation derived for the flow of a liquid on a planar plate[12]:

$$\mathrm{Re} = 4\Gamma / \eta_1 \,, \tag{3}$$

where $\Gamma = F_{\mathrm{B}}^0 / \varrho_1 \sum d$ is the density of wetting by liquid related to a length unit of the inlet edge. The character of the flow of a liquid on expanded metal is quite specific and cannot be compared with the flow on a planar wall or with the flow through a packed column. According to Kapica[13], the transition between the laminar and wavy region for a planar wall is given by a critical value of the Reynolds criterion:

$$\mathrm{Re_{crit}} = 2 \cdot 43(\delta_1^3/g v_1^4)^{1/11} . \tag{4}$$

From relation (4), it follows $\mathrm{Re_{crit}} = 15 \cdot 2$ for a n-butanol solution of nitrobenzene at 60°C ($\delta_1 = 31$ cm^3/s^2) and $v_1 = 0 \cdot 015$ cm^2/s) (ref.[8]). This means that the range in which reaction rates were measured in this work, *i.e.* up to Re = 14, belongs for the case of a planar wall fully to the laminar region. As a matter of fact, only viscous forces come into effect during pure laminar flow. From this reason, pure laminar flow may be assumed only up to approximately Re = 1·5 when the liquid trickles only ribs of the expanded metal. At 1·5 < Re < 3, expanded metal mesh become subsequently filled by the liquid film and at Re < 3 are the sheets completely covered by the liquid. It is therefore obvious that the character of the flow is determined by forces due to surface tension as well as by viscous forces. It follows from Fig. 3 that approximately from Re = 3, when the whole packing has been covered by the liquid, the hydrogenation rate of nitrobenzene is independent of the flow rate of the liquid. It means from the point of view of the gas transfer through the liquid that an increase in the mass transfer coefficient, which increases with Re, and an increase in the interface surface led to a more rapid absorption of the gas and, consequently, to the transition into the kinetic region of the reaction.

Reaction temperature. During all measurements in the flow reactor was the temperature of the gaseous stream measured by a thermocouple whose hot end was flowed around by the gas. Temperature oscillations reached maximally ± 1°C, which corresponds to temperature changes of the resistance heating in the reactor. The reactor may be thus considered to be an isothermal one.
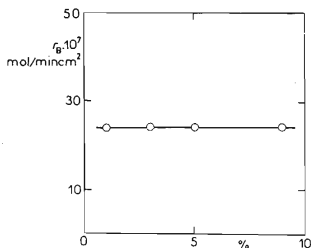

FIG. 4

Dependence of the Reaction Rate on the Nitrobenzene Concentration in n-Butanol (vol.%)
Re = 5, temperature 60°C, $p(\mathrm{H_2})$ = 1 atm.

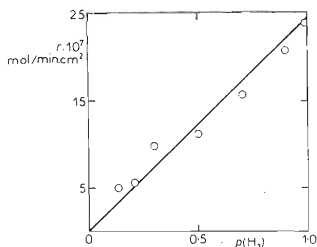
FIG. 5

Dependence of the Reaction Rate on the Partial Pressure of Hydrogen
Re = 5, temperature 60°C.

Kinetic region. The kinetic measurements in the flow apparatus were performed at a value of Re = 5, when the reaction rate was undoubtedly independent of the flow rate of the liquid. The dependence of the reaction rate on the nitrobenzene concentration in n-butanol was measured in pure hydrogen at 60°C. It is obvious from Fig. 4 that in diluted n-butanol solutions up to 10 vol.% nitrobenzene the reaction is of the zeroth order with respect to the substrate. All kinetic measurements were performed with solutions containing 5% nitrobenzene in n-butanol.

By calculations it has been found that the employed reactor is differential with respect to hydrogen. It has been also found from mass balance that the decrease in the hydrogen concentration at the end of the reactor amounts to 0·47 rel.% of the initial concentration and may be therefore neglected. The reaction rate with respect to hydrogen was determined by following the effect of the hydrogen concentration on the reaction rate. The hydrogen concentration was changed by dilution of hydrogen with nitrogen. The reaction is of the first order with respect to hydrogen, as it is seen on Fig. 5, and obeys the rate equation:

$$-r_B = k_T C_A / \varepsilon_A = k_T P_A / \varepsilon_A H_A . \qquad (5)$$

The temperature dependence of the reaction rate was measured at 35 − 80°C. Empty circles on Fig. 6 are experimentally measured values, full circles represent points corrected on the change in the hydrogen partial pressure due to increase in the vapour
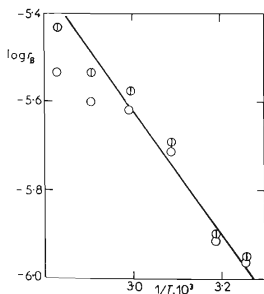

FIG. 6

Effect of Temperature on the Reaction Rate
Re = 5, $p(H_2)$ = 1 atm; ○ measured values, ◍ values corrected for the solvent vapour pressure.
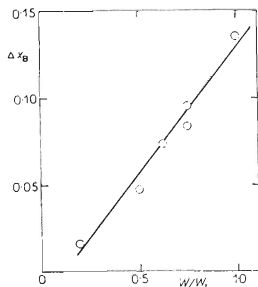
FIG. 7

Dependence of the Degree of Conversion on the Amount of Catalyst at a Constant Flow Rate of the Liquid
Re = 5, temperature 60°C, $p(H_2)$ = 1 atm.

pressure of the solvent brought about by increased temperature. Assuming validity of the Arrhenius relation, the activation energy of the reaction was calculated from the slope of the straight line on Fig. 6 passing through the full circles. A value of 6·4 kcal/mol has been obtained which agrees well with 6·3 kcal/mol as found by Acres and Bond[14] for a hydrogenation of nitrobenzene in the liquid phase with a catalyst containing 5% Pd on active carbon in a batch reactor. The rate constant of the reaction was calculated from the slope of the dependence of the reaction rate on the hydrogen partial pressure (Fig. 5) from Eq. (5). A value of Henry's constant $H_A = 2·48 . 10^5$ atm cm^3/mol[15,16] for the solubility of hydrogen in isobutanol at 60°C was employed for the calculation and it was found that k (233 K) = 1·82 cm/min. By connecting Eqs (1) and (5) it is possible to obtain an expression for the degree of conversion as a function of the amount of the catalyst:

$$\Delta x_B = k_T P_A W / \varepsilon_A F_B^o H_A . \qquad (6)$$

This dependence was investigated experimentally. The total packing of the catalyst $(W = 484$ cm$^2)$ was subsequently decreased to 20% of the original value. It is obvious from Fig. 7 that the straight line does not pass through the origin but that it cuts out a segment on the ordinate axis corresponding to 15% of the total packing. This part of the catalyst serves probably for refining the liquid substrate and the solvent, so that it becomes practically useless for the hydrogenation of nitrobenzene. The rate constant $k(233$ K) = 1·97 cm/min was calculated from the slope of the straight line on Fig. 7, which is in good agreement with the value evaluated from the dependence of the reaction rate on the partial pressure of hydrogen. The rate constant was further determined independently in the static apparatus. The initial concentration was 5 vol.% of nitrobenzene in n-butanol, the total amount of the liquid $V = 25$ ml. The catalyst was deposited on three expanded metal strips of the width of 2 cm, length of 6 cm, $W = 36$ cm^2. A mean reaction rate of 11·1 . 10^{-7} mol/min cm^2 determined in the steady state at 22°C, which corresponds to the rate constant calculated from Eq. (5) $k(295) = 0·94$ cm/min. Henry's constant at 22°C (ref.[9]) is 2·78 atm cm^3/mol. The rate constant extrapolated to this temperature from the measurements in the flow system (Fig. 6) is k (295 K) = 0·59 cm/min, which represents a fair agreement taking into account differences in the arrangements and different levels of the constant activity of the catalyst.

Transition and diffusional region. The hydrogenation rate of nitrobenzene decreases with increasing the flow rate of the liquid. It is brought about by a decrease in the hydrogen concentration at the catalyst surface. It follows from Fig. 3 that at a value of Re = 0·5, the lowest reaction rate $r_B = 11 . 10^{-7}$ mol/cm^2 min has been measured, which is approximately one half of that determined in the kinetic region. As, according to Eq. (5), the reaction is of the first order with respect to hydro-

gen, the hydrogen concentration at the catalyst surface is also one half of that in the kinetic region. It means that at low values of Re when the liquid trickles only ribs of the expanded metal, the hydrogen concentration at the catalyst surface assumes nonzero values and the reaction is not controlled exclusively by hydrogen transfer to the catalyst surface. In purely diffusional region, the concentration of the reacting gas A at the catalyst surface is equal to zero and the reaction rate is given by the relation:

$$r_{\mathrm{D}} = k_{\mathrm{A}(1)} C_{\mathrm{A}} / \varepsilon_{\mathrm{A}} = k_{\mathrm{A}(1)} P_{\mathrm{A}} / \varepsilon_{\mathrm{A}} H_{\mathrm{A}} . \tag{7}$$

It would be possible to obtain a theoretical value of the reaction rate in purely diffusional region from Eq. (7), to compare it with the measured values of the reaction rates and to estimate the degree by which experimental results measured at low values of Re differ from the purely diffusional region. This procedure would face the lack of knowledge of the value of the mass transfer coefficient for the transfer from the gaseous phase to liquid. The mass transfer coefficient for the expanded metal was measured by Kolář and Endršt[5], however, at considerably higher values of the Reynolds number ($67 < \mathrm{Re} < 670$). Results of these authors obtained for absorption of CO_2 in water with an expanded metal packing of the same geometry were extrapolated to low values of Re ($0.5 < \mathrm{Re} < 1$). Reaction rates calculated from Eq. (7) in this manner are approximately one hundred times lower than those measured in this work. Even though an extrapolation into the region of low Re values may lead to considerable error, it is obvious that the calculated values of reaction rates are substantially lower and that the hydrogenation of nitrobenzene does not proceed in purely diffusional region.

Finally it may be stated that rapid absorption of the gas in the liquid and good accessibility of the catalyst surface make it possible to conduct the reaction in the kinetic regime still at relatively low flow rates of the liquid. A disadvantage of the expanded metal as a catalyst carrier is the approximately ten times smaller specific surface of the active metal in comparison with other carrier catalysts, which leads to a high sensitivity to catalytic poisons. Despite this disadvantage, this type of the catalyst packing may compete with trickle-bed reactors containing pelleted catalyst, before all in cases of rapid reactions.

LIST OF SYMBOLS

C	concentration [mol/cm^3]	T	temperature [K]
D_{AB}	diffusion coefficient [cm^2/s]	V	volume [cm^3]
$\sum d$	length of the inlet edge [cm]	W	amount of catalyst [cm^2]
F	flow rate of liquid [cm^3/s], [mol/s]	Δx	degree of conversion
g	acceleration of gravity [cm/s^2]	ε	stoichiometric coefficient
H_A	Henry's constant [atm/cm^3 mol]	δ	kinematic surface tension [cm^3/s^2]
ΔH	heat of reaction [kcal/mol]	Γ	density of wetting [g/cm s]
$k_{A(1)}$	mass transfer coefficient [cm/min]	η	viscosity [g/cm s]
k_T	rate constant [cm/min]	ϱ	density [g/cm^3]
P	pressure [atm]	τ	time [min]
r	reaction rate [mol/cm^2 s]	ν	kinematic viscosity [cm^2/s]
Re	Reynolds criterion		

Indices

A	reacting gas	l	liquid phase
B	liquid substrate	o	initial value
D	diffusional region	t	total
g	gaseous phase		

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