HYDROGENATION OF NITROGEN OXIDE
ON PLATINUM-CARBON CATALYSTS IN ACIDIC MEDIUM

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Hydrogenation of nitrogen oxide in acid solutions on Pt–C catalysts proceeds in dependence on experimental conditions either in purely diffusion region or in the diffusion and kinetically controlled region. The boundary between these two processes shifts to the higher ratio of NO to H_2 partial pressures with increasing platinum content and decreasing intensity of agitation.

The previous works[1,2] reported on the hydrogenation of nitrogen oxide on platinum black. It was shown that under conditions which ensured that the hydrogenation process proceeded in the region of potentials $0.0 - 0.3$ V (RHE) and main hydrogenation products were hydroxylamine and ammonia, the rate of the overall process was controlled by the rate of transport of the dissolved nitrogen oxide to the catalyst surface. By contrast to this, Savodnik and coworkers[8] have proposed that on Pt–C catalysts the hydrogenation of nitrogen oxide to hydroxylamine proceeds in the kinetically controlled region, all the reduction products being formed by reactions of the common intermediate H_2NO. The aim of this work was to interpret in more detail the kinetics and mechanism of NO hydrogenation on supported Pt catalysts.

EXPERIMENTAL

Platinum-carbon catalysts were prepared in the following way. A carbon support was saturated by aqueous chloroplatinic acid solution, the suspension was stirred for two hours, dried on air at 60°C and platinum was reduced by hydrogen at 150°C for 6 h. The carbon support was PM-16-E carbon black (U.S.S.R.) graphitized at 2 700 or 2 420°C. The medium size of support particles was determined microscopically by measuring approx. 500 particles.

Procedure. For comparison of catalytic hydrogenation and electrochemical reduction rates, some measurements were made with the use of a tubular vessel, the lower part of which was equipped with a cylindrical platinum net with pressed catalyst (the overall geometrical surface 50 cm²), to which a capillary tube was attached, the upper enlarged part of which contained a reference hydrogen electrode. The constituent of the vessel was further an auxiliary platinum electrode which was separated from the main volume of the electrolyte by a glass diaphragm and also the inlet and outlet of gases and a glass stirrer. To ensure the sufficient strength of the working electrode, the catalyst was mixed with 5% PTFF and this mixture was then pressed on the net.

RESULTS AND DISCUSSION

Hydrogenation of nitrogen oxide by hydrogen in acidic medium on Pt–C catalysts produces, similarly to Pt black, three products: N_2O, NH_3OH^+ and NH_4^+. Typical dependence of the total hydrogenation rate r_t, the yield of N_2O and the potential of the catalyst suspension on the partial pressure of nitrogen oxide are shown in Fig. 1. It is seen that the total reduction rate is proportional to the relative pressure p_{NO}^{rel} (the total pressure $P = p_{NO} + p_{H_2} + p_{H_2O} = 0.1$ MPa and $p_{NO}^{rel} = p_{NO}/P$), analogously to the hydrogenation on Pt black[1]. By contrast to the latter, after attaining a certain hydrogenation rate, further increase in the relative NO pressure results in a sudden decrease in the hydrogenation rate, and that both in the total rate and in the rate of N_2O formation, and leads also to the strong potential increase.

The values of the critical pressure p_{NO}^{rel} $(p_{NO,c}^{rel})$ at which there occurs the decrease in the hydrogenation rate depends mainly on the content of the active metal in the catalyst and on the rate of stirring. Fig. 2 shows the dependence of the total hydrogenation rate related to one particle of the suspension on NO partial pressure for different Pt contents in the catalyst. Calculations of the number of particles in the reactor were made by using experimentally determined average sizes of support particles. It was assumed that the deposition of the metal does not influence the total
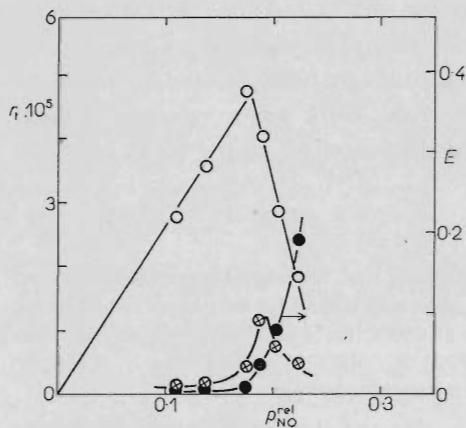

FIG. 1

Dependence of the rate of NO hydrogenation and of the potential of catalyst suspension on p_{NO}^{rel}, ○ total hydrogenation rate r_t (mol s^{-1} g$_{cat}^{-1}$), ● hydrogenation rate of N_2O formation (2 mol s^{-1} g$_{cat}^{-1}$), ⊗ the potential of suspension (V)
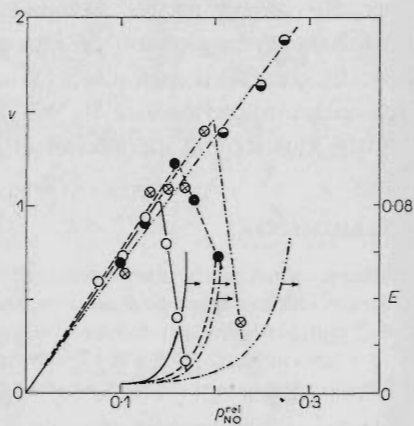
FIG. 2

Dependence of total hydrogenation rate v (mol s^{-1} n^{-1}) and of the potential of the catalyst suspension, E (V), on p_{NO}^{rel}, ○ 1% Pt, ● 5% Pt, ⊗ 10% Pt (experimental values multiplied by a factor of 1·87), ◒ 20% Pt

number of these particles. Fig. 2 demonstrates that the "critical" $p_{NO,c}^{rel}$ is shifted to higher values with increasing platinum content in the catalyst. Thus, for 1% Pt catalyst, the hydrogenation rate decrease occurs at $p_{NO}^{rel} \simeq 0.14$, for 5% at $p_{NO}^{rel} \simeq 0.16$, for 10% at $p_{NO}^{rel} \simeq 0.19$ and for 20% Pt catalyst this decrease was not observed even at $p_{NO}^{rel} = 0.28$. Also the potential of suspension at which the hydrogenation rate decrease is observed, depends on the Pt content. For the catalysts containing 1% and 5% Pt, the hydrogenation rate begins to decrease at $\Delta E \simeq 8$ mV, for 10% Pt catalyst at $\Delta E \simeq 20$ mV and for 20% Pt catalyst the hydrogenation rate does not decrease even at $\Delta E \simeq 55$ mV. Except for 10% Pt catalyst the hydrogenation rate r_t in the increasing part of the curve up to the critical pressure p_{NO}^{rel} does not depend on platinum content beyond experimental errors.

It was further studied how the intensity of stirring affects the dependence $r_t = = f(p_{NO}^{rel})$. From Fig. 3, which shows the total hydrogenation rate in dependence on p_{NO}^{rel} at different intensity of stirring, one can conclude that the decreasing intensity of stirring leads to a decrease in the slope of linear part of the curve and further shifts $p_{NO,c}^{rel}$ toward higher p_{NO}^{rel}'s. If maximal hydrogenation rate does not attain a certain value $\left(e.g.\ \text{for PM-16-E 2700} - 5\% \text{ Pt this value was } 4-5 \cdot 10^{-5}\ \text{mol s}^{-1}\ \text{g}_{cat}^{-1}\text{;}\right.$ $0 < p_{NO}^{rel} < 0.24$), the hydrogenation rate decrease does not occur. Similarly as critical $p_{NO,c}^{rel}$ shifts with decreasing intensity of stirring, also potentials of suspension shift in a similar way.

In previous work which concerned with the analysis of hydrogenation rate and the shape of polarisation curve of the electrochemical reduction of nitrogen oxide it was concluded that on Pt blacks the hydrogenation of NO proceeds to give NH_3OH^+ and NH_4^+ under conditions where the reaction rate is controlled by the rate of transport of the dissolved NO to the surface of reacting particles. Our further work[4] demonstrated that the electrochemical reduction of NO on Pt–C electrodes proceeds at a slower rate compared to Pt blacks, but − in spite of this − at $E < 0.3 - 0.25$ V the kinetics of the hydrogenation is so fast that on the rotating disc electrode at the rotation speed $\omega \leqq 1\,500$ min^{-1}, the process is controlled by the rate of NO transport to the electrode surface. In the present work the observed form of the dependence of the catalytic hydrogenation rate on the partial pressure p_{NO}^{rel} shows that at a certain p_{NO}^{rel}, at which one observes a sudden decrease in the hydrogenation rate, the reaction rate is no more controlled only by the rate of NO transport but that also the kinetics of the hydrogenation begins to play a role, and that even at very small $\Delta E \approx 10$ to 30 mV. With the aim to explain this fact in more detail, reaction rates of the hydrogenation and electrochemical reduction were measured in the same arrangement and under identical hydrodynamic conditions.

Fig. 4 shows the dependence of the rates of catalytic hydrogenation and electrochemical reduction on the electrode potential of the electrode prepared from PM-16-E 2700 − 5% Pt catalyst at maximal achieved intensity of stirring. The required potential of suspension in catalytic hydrogenation was adjusted by the choice of the ap-

propriate $p_{NO} : p_{H_2}$ ratio. For purposes of comparison with the rate of electrochemical reduction which was measured at $p_{NO}^{rel} = 1$, the experimental catalytic hydrogenation rate r_m was recalculated to $p_{NO}^{rel} = 1$ according to the realation $r_p = r_m/p_{NO}^{rel}$. From Fig. 4 it follows that the rate of the catalytic hydrogenation $(mol_{NO} \ s^{-1})$ is approximately 20 per cent higher than that of electrochemical reduction. The greater values for the catalytic hydrogenation rate are due to the fact that the current yields of the electrochemical reduction amount to only 90% because of the re-oxidation of the products on the auxiliary anode and also partly by the fact that as a consequence of the intense stirring used in the measurements, there proceeds a small spalling of the catalyst particles from the net, which particles act also as hydrogenation sites during catalytic hydrogenation. Reaction rates of both hydrogenation procedures are, however, approximately the same. Within the potential range $E \simeq 0{\cdot}0 - +0{\cdot}3 \ V$, the reaction takes place in the region of limiting diffusion current of the dissolved NO. In contradiction to the hydrogenation with the catalyst in suspension (Fig. 1), the decrease of the hydrogenation rate at higher p_{NO}'s has not been observed.

To explain the decreasing reaction rate of the catalytic hydrogenation, which — according to the shape of polarisation curve of the NO reduction[4] — should not occur since at these potentials the electroreduction takes place in the region of limiting
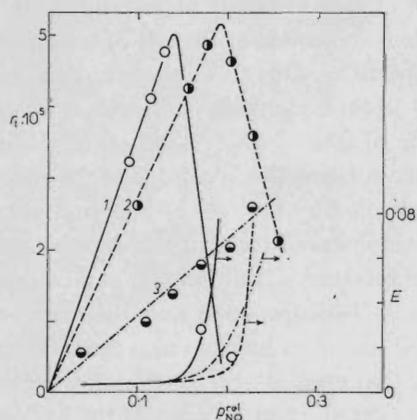

FIG. 3

Dependence of hydrogenation rate r_t (mol . $s^{-1} \ g_{-1}^{cat}$) and of catalyst potential on p_{NO}^{rel} for different intensity of stirring. The catalyst contained 5% Pt. The intensity of agitation increased in the sequence $1 < 2 < 3$

FIG. 4
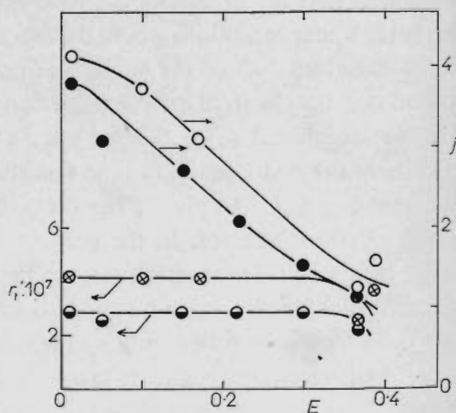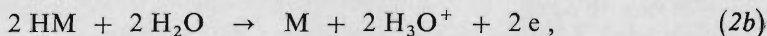
Dependence of the catalytic and electrocatalytic hydrogenation rate on the potential of the catalyst: O, ⊗ electrocatalytic rate r'_t (mol s^{-1}), ●, ◖ catalytic hydrogenation rate j (m s cm^{-2})

current so that also hydrogenation should not proceed in the diffusion-controlled region, we calculated the current density on the surface of a particle at the maximal hydrogenation rate. From measurements of particle sizes it can be concluded that the average particle size for the catalyst support used, *i.e.* graphite carbon blacks PM-16-E 2 700, is $1\cdot3 . 10^{-4}$ cm. Provided that we deal here with nonporous spherical particles, the specific surface is $2\cdot3$ m^2 g^{-1}. If for 5% Pt catalyst the maximal hydrogenation rate is $5 . 10^{-5}$ mol s^{-1} g^{-1}, then the reaction rate related to the particle surface of 1 cm^2 is $2\cdot17 . 10^{-9}$ mol s^{-1} cm^{-2}. If one presumes that for the reduction of NO to NH_3OH^+ and NH_4^+ the average number of transferred electrons n is $3\cdot5$, then the maximal current density is $7\cdot34 . 10^{-4}$ A cm^{-2}. On the rotating disc electrode[4] at $E \simeq 0\cdot00$ V, and similarly also on a tubular electrode (Fig. 4), the current density was $4 . 10^{-3}$ A cm^{-2}. On these electrodes at $E < 0\cdot3$ V the reduction proceeds in the region of limit current, under which conditions the inner layer of the catalyst does not participate in the reaction and the reduction takes place only on the developed external surface of the electrode. Let us assume further that the factor of roughness can change from 10 to 50. The actual current density changes within $i_1 = 4 . 10^{-4} - 0\cdot8 . 10^{-4}$ A cm^{-2}. From this it follows that the current density on the particle of suspension is approx. $1\cdot8 - 9$ times greater that the actual current density in the case of the electrochemical reduction on rotating or tubular electrode. The measured polarisation curves[4] correspond only to the conditions of hydrogenation represented by curve *3* in Fig. 3, in which case the decrease in the hydrogenation rate has not been found. For attaining the current densities of the electroreduction which would correspond to the conditions of catalytic hydrogenation (Fig. 3, curves *2* and *1*) it would be necessary to achieve substantially greater rates of stirring.

Catalytic hydrogenation can be regarded as the electrochemical process in the short-circuited galvanic cell, consisting of the cathodic reduction of nitrogen oxide

$$NO + n \, e \rightarrow (NO)^{-n}_{red} \qquad (1)$$

and of the anodic oxidation of hydrogen

$$H_2 \rightarrow 2 \, HM \qquad (2a)$$

$$2 \, HM + 2 \, H_2O \rightarrow M + 2 \, H_3O^+ + 2 \, e, \qquad (2b)$$

where $(NO)^{-n}_{red}$ stands for all the reduction products formed, *i.e.* N_2O, NH_3OH^+ and NH_4^+. Let us suppose that on platinum catalysts, similarly as on platinum, the slowest reaction is $(2a)$; then for the rate of anodic hydrogen oxidation one can write the relation (3).

$$i = nFk_a c_{H_2} \Theta_M^2 - nFk_c \Theta_{MH}^2 \qquad (3)$$

The potential of the catalyst is controlled by the degree of its coverage by adsorbed hydrogen Θ_{MH} according to the relation (4)

$$E = E_s^0 + RT/F \ln (\Theta_M/\Theta_{MH}),\tag{4}$$

where E_s^0 is the standard potential of the adsorption reaction of hydrogen atoms. At the equilibrium

$$E_r = E_s^0 + RT/F \ln (1 - \Theta_0)/\Theta_0,\tag{5}$$

where Θ_0 is the equilibrium coverage of the surface by hydrogen in currentless state. The exchange current density of the reaction can be then expressed by Eq. (6).

$$i_0 = nFc_{H_2}^0(1 - \Theta_0)^2 = nFk_c\Theta_0^2\tag{6}$$

Combination of Eqs $(3)-(6)$ leads to the relation for the current density $(\text{Eq. }(7))$

$$i = i_0\{1/[\Theta_0 + (1 - \Theta_0)\exp(F(E - E_r)/RT]^2 \cdot$$
$$\cdot c_{H_2}/c_{H_2}^0[\exp(2F(E - E_r)/RT) - 1]\}.\tag{7}$$

Let us assume for simplification that $E_s^0 = E_r$; then $\Theta_0 = 1$, which leads to relation (8).

$$i = i_0 c_{H_2}/c_{H_2}^0 (\exp(2F(E - E_r)/RT - 1).\tag{8}$$

This expression is valid in the case that only hydrogen adsorbs on the electrode, *i.e.* under conditions where the rate of cathodic process (NO reduction) is so fast that it occurs in the diffusion controlled region and the concentration $c_{NO}^p = 0$. This condition is fulfilled in the p_{NO}^{rel} region in which the dependence $r_t = f(p_{NO}^{rel})$ is linear with the positive slope. In such a region it holds that

$$nFr_t = nFkD_{NO}p_{NO}^{rel}/\delta = I = i_0 Ac_{H_2}/c_{H_2}^0(\exp(2F(E - E_r)/RT - 1),\tag{9}$$

where r_t is the total hydrogenation rate, k is the coefficient of proportionality between p_{NO}^{rel} and c_{NO}, D_{NO} is the diffusion coefficient of dissolved NO, δ is the thickness of the diffusion layer, I is the current of the hydrogen oxidation, A is the effective catalyst surface. By modification of Eq. (9) one obtains the relation between the catalyst potential and the nitrogen oxide partial pressure $(\text{Eq. }(10))$.

$$\Delta E = (E - E_r) = RT/2F \ln (c_{H_2}^0/c_{H_2}) + RT/F \ln [(nFkDp_{NO}^{rel}/\delta i_0 A) + 1].\tag{10}$$

The first member of the right side of the equation represents the potential change

due to the difference between the hydrogen concentration on the catalyst surface and the equilibrium concentration of the reference hydrogen electrode, the second term is the activation over-voltage of the hydrogen oxidation reaction. Using the known Henry constants of the solubility of hydrogen and nitrogen oxide[5] and diffusion coefficients of these compounds in water[6] for the final composition of the product, we calculated the concentration over-voltage of hydrogen for $p_{NO}^{rel} = 0.1$ to 0.3. The values are relatively small — for $p_{NO}^{rel} = 0.2$, $E_p = 6$ mV, for $p_{NO}^{rel} = 0.3$, $E_p = 10$ mV. From Figs 2 and 3 it follows that in the p_{NO} region up to $p_{NO,c}^{rel}$ the hydrogen concentration and the activation over-voltage of hydrogen are approximately the same. From Eq. (10) one can conclude that at a given p_{NO}^{rel} the ΔE value will decrease with increasing activity of the electrode (the greater i_0) and with increasing development of the surface, i.e. with increasing ratio of the effective to geometrical surface.

After $p_{NO,c}^{rel}$ is exceeded, $c_{NO}^p \neq 0$ and one has to consider also adsorption of the reactant NO or of the intermediate NOH on the catalyst surface. This process reduces the surface available for the hydrogen oxidation to the value given by the expression $A' = A(1 - \Theta_{NO})^2$. At the same time, also for the cathodic reduction of NO, in place of the simple expression for the limit current density one has to use the relation for the dependence of the current density on the potential, taking into account the NO concentration difference between the catalyst surface and the electrolyte volume. In contradiction to Eq. (10), the dependence of p_{NO}^{rel} on the potential of catalyst suspension cannot be described by a simple relation. It can be stated only qualitatively that after p_{NO}^{rel} is exceeded, a part of the catalyst is blocked by the unreacted NO. This results in the decrease in the effective surface of the electrode and, in agreement with Eq. (10), also in the decrease in the potential of suspension, ΔE. The ΔE decrease induces the rate decrease of NO reduction, so that for each p_{NO}^{rel} a certain stationary state is established. It is worthy of note that the $p_{NO}^{rel} > p_{NO,c}^{rel}$ region is considerably unstable, since already small p_{NO}^{rel} increase leads to the great and fast ΔE decrease. On the other hand, the displacement of adsorbed NO by increasing $p_{H_2}^{rel}$ is very slow and the ΔE of the catalyst suspension decreases very slowly, especially at $\Delta E \geq 0.1$ V.

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