

EFFECT OF IONIZING RADIATION ON SUPPORTED CATALYSTS OF Ni-ZnO TYPE IN MALEIC ACID HYDROGENATION

Rostislav KUDLÁČEK and Hana SOLAŘOVÁ

*Department of Nuclear Chemistry,
Czechoslovak Technical University, 115 19 Prague 1*

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A silica supported nickel-zinc oxide mixed catalyst was modified in different stages of its preparation by preliminary treatment with ^{60}Co gamma rays. The investigation was performed aimed to find such a composition and preparation procedure which would guarantee a satisfactory catalyst activity in the maleic acid hydrogenation. Possible explanation is offered for the change in activity observed after the irradiation of the catalyst. The precipitation step and the activation of the catalyst with hydrogen which is carried out after the reduction of the mixed oxide, have been found to be the stages determining the activity of the catalyst.

Preliminary irradiation of the catalyst (especially of supported sort) requires to select such types of rays, modes of irradiation and adsorbed dosages which lead to a substantial increase in the catalyst activity and reaction rate. Catalyst treatment of this kind has been applied both in the gas phase and in the liquid phase reactions. In the latter case, the papers of the group of Sokolskii are of special importance. This group has concentrated primarily on gamma-alumina supported catalysts of the platinum group which are irradiated either just before the beginning of the reaction or the catalyst support itself is irradiated before the deposition of the active component. Thus, a 0.5% platinum catalyst¹ exhibited 4.5 times higher activity after the treatment with neutrons with the particle fluence 10^{17} cm^{-2} . The catalyst with a higher platinum content (5%) gave after the irradiation $10\times$ higher activity in the hydrogenation of 3-hydroxy-3-methyl-butane, while the activity of the comparable palladium catalyst increased, in this case, only $3\times$ and with the similar rhodium catalyst only twice. The described changes are usually explained by modification of size of the support-pores, resulting from the irradiation². A catalyst of the same type was used also for investigation of the effect of addition of fluorine and lithium, both of which are being transmuted in the course of the irradiation. The resulting increase of reaction rate is in this case smaller due to the induced activity³. Ionizing rays influence positively the catalyst resistivity against catalytic poisoning⁴; the poisoned platinum, palladium and rhodium catalysts were regenerated⁵ after their irradiation in the nuclear reactor, (in all cases, the samples were supported on gamma-alumina and poisoned with methylthiophene). Remarkable effect of preliminary treatment of the alumina supported platinum catalyst, with ^{90}Sr beta-rays, was shown in papers⁶⁻⁷. An analogical positive effect was observed with the alumina supported Rh-Pt-Fe mixed catalyst, in the hydrogenation of cyclohexene^{6,8}, after the catalyst had been treated with alpha particles. The gamma rays from the ^{60}Co source effect positively both the palladium and the platinum catalysts, independently whether the support itself⁹ or the final catalyst¹⁰ was irradiated (in both papers the cyclohexene, nitrobenzene and phenylacetylene were hydrogenated).

This paper has been aimed to determine to which extent the activity of the sup-

ported hydrogenation nickel-zinc oxide catalyst is affected by the ionizing gamma rays. The obtained results permit to specify which preparation stages are crucial for the final activity of the catalyst.

EXPERIMENTAL

Three sets of samples of silica supported Ni-ZnO catalyst were prepared. The samples and solutions were prepared from nickel(II) nitrate, zinc nitrate, potassium carbonate, sodium hydroxide (all of R.G. purity) using tridistilled water. The silica support was supplied by Severočeské tukové závody and fitted the Czechoslovak Standards TPN-28-461. Electrolytic hydrogen, prepared in a laboratory electrolyzer, was purified with a deoxidizing catalyst. In the course of preparation of the catalyst, the nickel(II) nitrate and zinc nitrate solutions were mixed in such proportions that the resulting active component contained 42% (mol) nickel oxide and 58% (mol) zinc oxide (a non-supported sample of this composition showed in the maleic acid hydrogenation the highest activity¹¹). The solution was then contacted with a given amount of silica and nickel and zinc were then precipitated with a 15% excess of carbonate.

The formed carbonate precipitate was decanted until no further reaction of nitrate ions was detected. After filtering and rinsing with redistilled water, the precipitate was dried for 1 hour, at 130°C, in the air (the calcination conditions are given for each individual sample set, below). The reduction of the calcinated samples, respectively the reductive decomposition of the carbonate in hydrogen (reductive calcination) were performed with electrolytic hydrogen. The reduction and the reductive calcination were carried out in the reaction vessel just before the beginning of the reaction (see below).

With the first set of samples, we have changed the ratio of the active component and the support. Four samples were prepared in this group with the following active component contents: K1 — 100%, K2 — 70%, K3 — 50%, K4 — 30%. After the calcination, each of the samples was irradiated with a 10^6 Gy gamma dose. The samples of the second set had all identical composition with the sample K2. Sample B was prepared on a support which was pretreated with a 10^6 Gy dose, sample A was made on a non-irradiated support. The precipitation of the samples of the first and second set (lasting several minutes) and their decantation proceeded at laboratory temperature. After the drying and calcination for 5 hours, at 400°C, in the air, the samples were left for several hours in the cooling-down furnace. The samples of the third set had identical composition with the samples of the second set but their preparation resembled the preparation technology of the industrial nickel catalyst (Severočeské tukové závody). The solution of the nickel and zinc salts was precipitated with potassium carbonate at 80°C during three hours (silica was added into the initial solution after the temperature has reached 50°C). The sample was then stirred for 4 hours at the temperature of the boiling point of the suspension. In this way we have prepared the third set of samples on the irradiated support. The samples are presented in the sequence of their preparation and with the corresponding irradiation dosages in the brackets: 1 (non-irradiated), 2 (10^4 Gy), 3 (10^5 Gy), 4 (10^6 Gy), 5 (non-irradiated). A MPX-gamma $100\text{ }^{60}\text{Co}$ source was used in all cases.

The maleic acid solution (2-butenedioic acid (z)) was prepared in a 0.1 mol l^{-1} concentration and the final pH value was fitted with sodium hydroxide. The apparatus used and the procedure by which the hydrogenation rate of the maleic acid in water solution was measured have been described in paper¹¹. Unless stated otherwise, the following conditions were used in the reaction proceeding in the kinetic region: the reaction temperature $25 \pm 0.1^\circ\text{C}$, the agitation frequency 380 c/min, the solution volume 7 ml, the hydrogen pressure $9.67 \cdot 10^4$ Pa, the catalyst weight less than 15 mg. The apparatus was calibrated in such a way that the hydrogen deficit from the

maleic acid hydrogenation (measured from difference in oil-manometer levels) was compensated with the hydrogen from the gas burette. From the time-dependence of the manometer-level changes (measured for 15 minutes), we have calculated the rate of the hydrogen consumption. The obtained value has been used for evaluation of the reaction rate, expressed as the amount of hydrogen consumed per a unit time and nickel weight.

The reaction rate, the activation energy and the error in determination of both former parameters, from the experimental data, were evaluated numerically, applying the least squares analysis. The amount of maleic acid adsorbed on the catalyst under conditions comparable with the reaction threshold was determined polarographically¹², using a phosphate buffer, from the acid concentration difference before and after the sorption. The adsorbed amount was expressed as the weight of the adsorbed acid per a unit weight of the catalyst. The time-courses of the reduction and reductive calcination, as well as, the reduction degree of nickel(II) oxide in hydrogen, in these two processes, were determined from the solid-phase weight-deficit at constant temperature. The instantaneous sample weight was measured with the accuracy ± 0.1 mg for the total sample weight 50 mg. The reduction degree was expressed by ratio of the weights of the oxide in the catalyst, before and after the reaction. Specific surface of the samples was determined by selective nitrogen adsorption and desorption from the hydrogen-nitrogen mixture. The size of the specific surface area (given simply by the amount of nitrogen adsorbed at liquid nitrogen temperature), per a unit sample weight, was measured by means of the titanium(IV) oxide standard with specific surface $S = 7.16 \text{ m}^2 \text{ g}^{-1}$. The sample microstructure was determined by the Debye-Scherrer method, using a commercial apparatus HZG 3 (Freiberger Präzisionsmechanik).

RESULTS AND DISCUSSION

The unsupported mixed nickel-zinc oxide type catalyst exhibited reasonable rates and good resistivity against thermal treatment during the hydrogenation, in the cases, where the concentration of zinc oxide exceeded 30 (mol) % (ref.¹¹). In the case where the active component was deposited on the silica support, the reaction rate of all samples depended on temperature of the reduction (samples of the first set, reduction time 80 minutes, pH of solution 5.2–5.4). The reaction rate of the unsupported sample K1 did not depend (as it was in the previous case¹⁰) considerably on the reduction temperature, within the studied temperature range. This fact proved again the stabilizing influence of the zinc oxide. Independently on their composition, the supported catalysts of the first group showed a non-linear behaviour in their reaction-rate dependence on reduction temperature. One can therefore conclude that it is possible to find such a temperature range for the reduction in which the reaction rate (defined as above) is higher with the supported catalyst than with the non-supported one. The reason why the reaction rate of the samples of the first set depends on the reduction temperature cannot be explained only by the existence of two competing processes, due to which the increased temperature of the sample heat treatment in hydrogen increases the number of the reduced nickel atoms but, simultaneously, it leads to destruction of the active centres.

The presence of the support raises the minimum temperature which is required to obtain the reduced catalyst in stationary conditions. At lower temperature, one

can see with the supported samples, an interaction between the samples and the solution. This interaction results in a deflection from linearity of the hydrogen-consumption time-dependence, from the very beginning of the reaction onset. The lesser reduction extent (Table I) indicates that the increasing support content decreases substantially the number of the reduced nickel atoms. The reduction degree of each sample was measured after 15 minutes of reduction. This time was sufficient to obtain the final values of the reduction degree but it was not long enough to reach stable catalytic activity. Table I also gives, for all samples, the surface-area values for the reduced, in the air passivated catalysts (the applied experimental procedure does not permit to measure the surface area of the reduced, pyrophoric sample). The reaction rate ratio of the non-supported sample and the sample with a varying silica content does, therefore, depend neither on the reduction degree nor on the size of the surface area.

Another possible reason for the observed activity changes can be connected with the modification of the microstructure. In our measurements we have observed¹¹, with a number of non-supported Ni-ZnO type catalysts (for different contents of individual components within the measured region), a number of weak lines in the Debye X-ray diffraction pattern, which have been very difficult to interpret. Silica itself gives in the measured diffraction region a very complex spectrum. This background spectrum disturbs severely the actual measurements of the deposited nickel-zinc oxide samples which, again, cannot be measured in the reduced form. It was impossible to evaluate the obtained spectra of the K2, K3 and K4 samples, in a way, which would allow to decide whether the presence of the silica support affects the lattice constant of the active component or not.

TABLE I

Properties of the samples of first set

| Sample | Reduction degree % | Temperature °C | Surface m ² g ⁻¹ |
|--------|-----------------------|-------------------|---|
| K1 | 100 | 440 | 14.51 |
| K2 | 27 | 440 | 45.49 |
| K3 | 20 | 470 | 24.25 |
| K4 | < 5 ^a | 470 | 16.82 |

^a No measurable mass deficit was detected for this sample; reduction: 15 minutes; surface measurement: after the reduction (80 minutes, at 470°C), the sample was left to cool down to laboratory temperature and passivated with air.

With the catalysts of the first group, we have studied also the effect of preliminary irradiation of the calcinated samples, before their reduction, using adsorbed doses 10^7 Gy of gamma rays. For solutions with pH 5.6–5.7 (in which maleic acid is dissociated in major to the first degree), the irradiation of the samples led in all cases to higher reaction rates. This increase was getting smaller with the higher reduction temperatures (the temperature range was comparable with Fig. 1) and with the increasing support content. In no case exceeded this increase 10%. On the other hand, for solutions with pH 12.1–12.3 (in which practically only ions of the second dissociation degree are present), the irradiated samples were less active and the difference between the non-irradiated and irradiated samples again did not exceed 10%. It has been verified that the reaction course in the acidic and the basic region is not similar due to the earlier described¹¹ difference in the rate-limiting stage. In the first case, the reaction course is determined by the adsorption of the organic substrate, in the second case, by the sorption of hydrogen – regardless whether the mixed oxide is supported or not.

The relatively little change in reaction rate caused by preirradiation of the calcinated sample, as well as, the fact that the supported mixed nickel-zinc oxide catalyst was active in the maleic acid hydrogenation, led to our decision to find out with the samples of the second group, how far the final activity of the catalyst is affected in the case when only the support itself is irradiated. Sample B, prepared on the support which was treated with a 10^7 Gy dose, gave in comparison with sample A (non-irradiated support) higher reaction rate. The reaction rate of both samples increased with the temperature, within the studied temperature range 408–472°C. In this temperature range, the sample prepared on a pretreated support was reduced to a higher extent and this difference was getting larger with the increasing tempera-

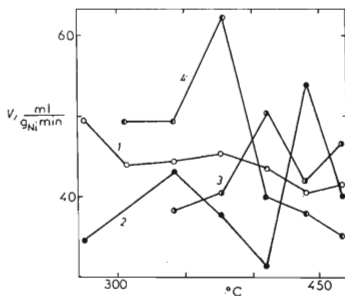


FIG. 1

Dependence of the hydrogenation rate on reduction temperature. Time of reduction 80 minutes; time of calcination 5 hours; temperature of calcination 400°C; samples of the first set: 1 K1, 2 K2, 3 K3, 4 K4 (for details see Table I)

ture (Table II). The surface area size of the unreduced samples A and B equalled $57.5 \text{ m}^2 \text{ g}^{-1}$ and $47.5 \text{ m}^2 \text{ g}^{-1}$, respectively. In order to examine closer the increase in activity of the sample B (with respect to sample A), we have measured the dependence of the hydrogenation rate on the reaction temperature (Fig. 2). The catalyst which was prepared on the irradiated support (sample B) showed within the whole temperature range higher reaction rates. However, in the region in which the reaction rate is limited by the addition of hydrogen, we found no difference in the activation energies exceeding the error of measurement, nor a marked difference in the frequency factor values. From that part of the dependence in Fig. 2 in which the hydrogenation process is limited by the hydrogen addition, we have calculated the activation energy $E_A = 44.4 \pm 10 \text{ kJ/mol}$ for sample A and $E_B = 42.3 \pm 10 \text{ kJ/mol}$ for sample B and the corresponding frequency factor values $A_A = 1.63 \cdot 10^9$ and $A_B = 0.77 \cdot 10^9$. The increase of reaction rate observed with the sample which was prepared on the irradiated support, in the solution composition region with pH 5, can be probably explained by higher amount of the adsorbed organic compound. This is suggested by the comparison of the dependence of reaction rate on reaction temperature, for the irradiated and non-irradiated sample (Fig. 2). With increasing temperature,

TABLE II

Reduction degree of the samples of second set

| Temperature, °C | 380 | 410 | 440 | 470 |
|---------------------|-----|-----|-----|-----|
| Reduction degree, % | | | | |
| A | 27 | 36 | 38 | 40 |
| B | 29 | 41 | 46 | 51 |

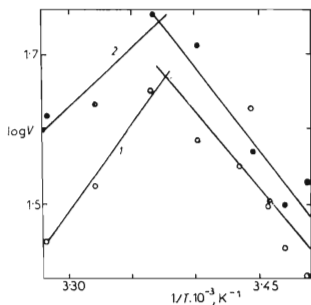


FIG. 2

Dependence of the hydrogenation rate on reaction temperature. The solution pH 5.5; time of reduction 80 minutes; temperature of reduction 470°C ; samples of the second set: 1 A (non-irradiated) 2 B (irradiated)

the reaction becomes limited not by the hydrogen adsorption (right-hand part of the dependence) but by the adsorbed amount of the reacting substrate (left-hand part of the dependence). The point of intersection, which is given by the amount of the adsorbed organic compound (at $3.37 \cdot 10^{-3} \text{ K}^{-1}$), is found with the irradiated catalyst at higher reaction rates.

The technology of preparation of the samples of first and second set, especially then the precipitation at laboratory temperature (lasting several minutes) and the long calcination process, lead to relatively low activity of the final catalyst. The adherence of the active-component intermediate to the support occurs, for the supported nickel catalyst, after the precipitation ("the precipitation deposition"¹³). The character of the precipitate which was obtained at the increased temperature of the initial solution (around 80°C) is different¹⁴. Proper adherence of the precipitate to the support requires to apply at the end of the precipitation, an additional several-hour-lasting heat treatment of the sample, at the temperature of the boiling point of the suspension (see¹⁴). This experience obtained with the support nickel catalyst was used also for the studied nickel-zinc oxide catalyst. On the samples of the first and second set we have observed visually clean particles of the support on which no catalyst was deposited. Based on the obtained results, we have prepared the samples of the third set which enabled us to study the effect of the preliminary support treatment with gamma rays.

One could expect that the subsequent heat treatment of the sample which was exposed to gamma rays will reduce the effect of the irradiation. For this reason, we have focused at first our attention on finding the minimum temperature which can be applied during the last stage of sample preparation and on duration of such a treatment. For that technology in which the dried up hydrocarbon is, first, decomposed in the air and then reduced with hydrogen, we have investigated the minimum time required for sufficient calcination of sample 1:

| | | | |
|---|-------|-------|-------|
| time of calcination, minutes | 30 | 45 | 60 |
| reaction rate, ml/g _{Ni} minutes | 148.7 | 136.9 | 118.7 |

As one can see, the sample exhibits after 30 minutes of heat treatment reasonable hydrogenation rate and this rate decreases with the prolonged calcination. Samples of the third group give up to three times higher hydrogenation rates in comparison with the two preceding groups. This indicates that the low-rate precipitation at higher temperatures, the subsequent heat treatment of the obtained suspension and the minimum time of calcination, have all remarkable effect on the final activity. At the maximum temperature 470°C which we were able to apply in our glass system, we have measured the dependence of the sample activity on reduction time, for the samples of identical composition but differing in the irradiation dosages (Fig. 3). The

values which were obtained with samples reduced for less than 70 minutes are not given because these samples did not possess stable activity (*i.e.* these samples interacted with the solution). The change of the hydrogenation rate with dosage is, for equal reduction time, non-monotonous and the hydrogenation rate both of the irradiated and non-irradiated samples depends strongly on the time of the reduction. Such behaviour, probably, points at a very complex kinetics of formation and destruction of the active centres. The reaction rate dependence on the dosage is characterized, for low reduction time values, by the maximum at 10^5 Gy, a slight increase at 10^4 Gy and decreasing trend for the highest dosages. For high reduction time values, the maximum rate is obtained at 10^4 Gy, and both higher dosages lead to the decrease of hydrogenation rate. The change in character of the described dosage dependences indicates different resistivity of the irradiated samples against the heat stress to which the samples are exposed during the reduction (this process is practically completed after 15 minutes) and during the subsequent sample interaction with hydrogen, at given temperature. For the reduction time 90 minutes (at this value the biggest difference in activity was observed after the irradiation of the support), we have measured the reaction rate dependence on reduction temperature. From the character of this dependence (Fig. 4), it is possible to see that with the increasing temperature, the hydrogenation rate does not decrease and no annealing is observed which would weaken the effect of the preirradiation. All samples showed again a distinct non-monotonous character in the investigated dependence, marked with two maxima

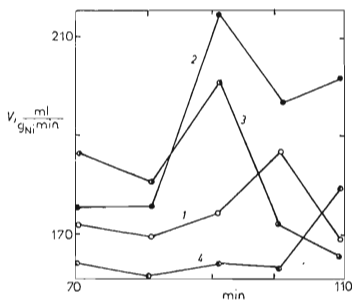


FIG. 3

Dependence of the hydrogenation rate on reduction time. Temperature of calcination 420°C ; time of calcination 30 minutes; temperature of reduction 470°C ; samples of the third set: 1 1, 2 2, 3 3, 4 4

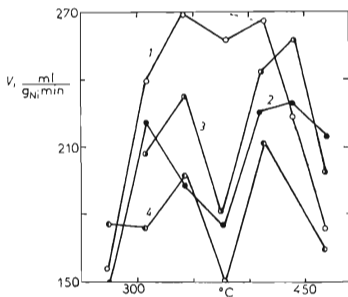


FIG. 4

Dependence of the reaction rate on reduction temperature. Temperature of calcination 420°C ; time of calcination 30 minutes; time of reduction 90 minutes; pH 5.5; samples of the third set: 1 1, 2 2, 3 3, 4 4

and a significant minimum. Also the dependence on the dosage has changed its character: at low temperature, the reaction rate decreases with the dosage. At medium range temperatures, the reaction rate is higher in the maxima region with the 10^5 Gy dosage then with the 10^4 Gy dosage. On the other hand, in the highest temperature range, the largest reaction rate is obtained for the 10^4 Gy dosage.

Extensive modification of the catalyst by preliminary gamma-ray support-treatment has been evidenced also by the reaction rate dependence on reduction temperature of the calcinated sample, obtained for a different solution composition with pH 12. This solution contains only ions of the second dissociation form A^{2-} and the rate limiting step is given, in such a case, by the sorption of hydrogen. For samples 1 and 4 of the third set, we have measured the difference in their reaction rates (both these samples showed the largest difference in analogical dependence of the samples prepared similarly at pH 6 (Fig. 5)). The remarkable dependence of the activity of sample 4, on heat treatment, indicates that the preliminary support irradiation modifies the final active centres — on the formation of which hydrogen, evidently, participates.

In order to reduce the effect of the heat treatment in the last preparation steps, we have tested on the samples of the third set the possibility of combining the steps of calcination and reduction into one process, possibly called „reductive calcination”. The reaction-rate time-dependence of the sample treated in such a way (at 470°C) has two characteristic regions: in the range 80–90 minutes and 100–110 minutes (Fig. 6). Such behaviour is evidently connected with the fact that in the above pro-

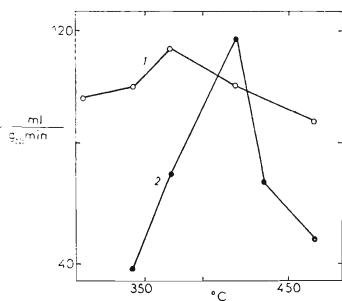


FIG. 5

Dependence of the hydrogenation rate on reduction temperature. Time of reduction 90 minutes; temperature of calcination 420°C ; time of calcination 30 minutes; pH 12.2; samples of the third set: 1 1, 2 2

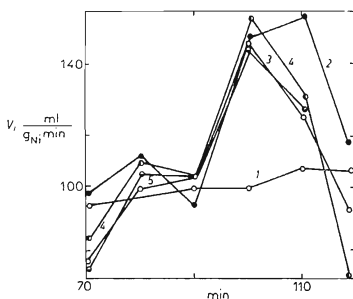


FIG. 6

Dependence of the hydrogenation rate on time of the reductive-calcination. Temperature of reductive-calcination 470°C ; pH 5.5; samples of the third set: 1 1, 2 2, 3 3, 4 4, 5 5

cess, the relative effect of calcination and reduction is not the same for different preparation-times of the final catalyst, despite the fact that these two processes are actually overlapping. Longer sample treatment in hydrogen results in thermal destruction of the active centres, as one can deduce from the large decrease of reaction rate for the reductive-calcination time 120 minutes. Sample 3 differs from the above described character of the reaction-rate time-dependence which is characterized by a maximum and two steps. The activity of this sample remained lower, compared with the non-irradiated sample, even when the temperature of reductive-calcination has been reduced (Fig. 7). In this case (unlike in the analogical dependence obtained with the samples which were calcinated and reduced separately), no significant maximum is observed but the course of the dependence is in no way simply monotonous. The process of reductive-calcination evidently leads to a final catalyst which is not identical with the similar product obtained by separated calcination and reduction. Such a conclusion is evident from the comparison of the time, the temperature and the dosage dependences of the samples which were prepared in both ways.

The reaction rate measurements (Fig. 3), the character of the reductive-calcination courses and the surface area measurements (Table III) have shown that samples 1 and 5 (which were both prepared on a non-irradiated support as the first and last member in the sequence) are identical and the differences between the samples 1, 5 (respectively 2, 3, 4) are, therefore, caused by modification of the support with gamma rays.

The preliminary support irradiation leads also to changed values of some parameters of the prepared samples or their intermediates. These parameter changes have been therefore considered as a possible explanation for the observed catalytic activity changes. The support-surface-area, however, decreases with the increasing size of the adsorbed doses (Table III) so that the resulting

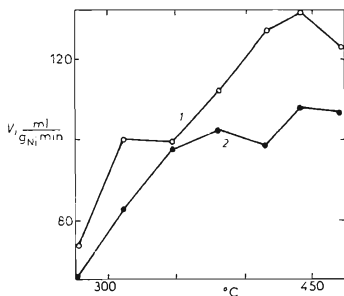


FIG. 7
Dependence of the hydrogenation rate on temperature of the reductive-calcination. Time of reductive-calcination 110 minutes, pH 5.5; samples of the third set: 1, 2, 3

change in activity cannot be attributed to the change of this geometrical factor. The surface area of the calcinated supported samples is a non-monotonous function of the increasing dosage (Table III) and thus, again, it cannot be simply correlated with the described support-surface-area changes. The amount of adsorbed maleic acid depends on the dosage (for both solution composition regions — Table III) in a different way than does the reaction rate. Another factor which can possibly influence the activity is given by the number of the reduced nickel atoms, which itself depends on the reduction degree reached during the reduction or reductive calcination. The reduction extent increases steadily with the increasing size of adsorbed doses (Table III) and reaches its limiting weight-deficit value after 12–15 minutes.

The comparison of changes in the dependences of the above mentioned surface parameters (the amount of adsorbed acid and the number of reduced atoms), on the adsorbed dosage, leads to the conclusion that these parameters cannot be in a simple way mutually correlated. Consequently, these changes cannot be significant for the support modification by the preirradiation, at least, as far as the catalytic activity is concerned. Similar lack of correlation can be found also for the reaction rate dependence on the adsorbed dosage, observed with catalysts of different origin and for different compositions of the acid solution. The dominant parameter which determines the catalytic activity of the supported samples is the interaction of the samples with hydrogen after the reduction, where the temperature and the duration of this interaction are the decisive factors (the reduction itself is considerably shorter than is the time required for attaining stable and satisfactory activity). The irradiated samples show an analogical non-monotonous character of the hydrogenation rate dependence on the length and temperature of the heat treatment in hydrogen. This

TABLE III
Properties of the samples of third set

| Sample | Adsorbed dosage Gy 10^4 | Surface, $m^2 g^{-1}$ | | Extent of reductive calcination % | Adsorbed amount of maleic acid, $g g^{-1}$ | |
|--------|------------------------------|-----------------------|------------|--------------------------------------|--|---------|
| | | support | calcinated | | pH 5.5 | pH 12.6 |
| 1 | 0 | 7.2 | 80.3 | 29 | 0.261 | 0.293 |
| 2 | 1 | 6.2 | 90.3 | 37 | 0.220 | 0.215 |
| 3 | 10 | 5.5 | 84.6 | 45 | 0.227 | 0.226 |
| 4 | 100 | 4.7 | 96.2 | 48 | 0.020 | 0.498 |
| 5 | 0 | 7.2 | 81.7 | 27 | — | — |

The surface was determined on samples which had been calcinated for 30 minutes at $420^\circ C$. The weight of the samples before the reductive calcination was 50 mg, the temperature in determination of the degree of reductive calcination was $415^\circ C$. For measurement of the adsorbed amount, the sample was calcinated for 30 minutes at $420^\circ C$ and before the sorption reduced for 90 minutes at $470^\circ C$.

proves unambiguously that the shape of the dependence (which is marked with extremes) is not accidental. Another evidence for the existence of such a regularity can be drawn from the fact that at temperatures corresponding to the extremes on the reaction rate curves, the dependence on the dosage also changes its character — independently which one of the two preparation ways of the final catalyst was used. In spite of the fact that the irradiation of the support before deposition of the active component changes the properties of all the intermediates, the resulting activity is affected only in such a way that the samples show different sensitivity in their interaction with hydrogen, in the last step of preparation. The basic character of modification of the activity by the sample treatment with gamma rays is connected neither with the change of geometrical surface during the individual stages of the catalyst preparation, nor it depends on the varying amount of the organic substrate adsorbed from the solution or on the number of reduced nickel atoms. On the other hand, the nature of this modification is related to the character of the reactive centres and to the changes of their energy states. This assumption is supported also by comparison of the reaction rate dependence of samples 1 and 4, respectively of their activation energies and frequency factors calculated from these rates. For the solution composition with pH 12, the apparent activation energy values calculated from the Arrhenius equation $E_1 = 29.3 \pm 3 \text{ kJ/mol}$ for the non-irradiated sample and $E_4 = 46.4 \pm 7 \text{ kJ/mol}$ for the irradiated sample. The corresponding frequency factors are $A_1 = 1.6 \cdot 10^6$ and $A_4 = 1.6 \cdot 10^{10}$.

Based on interpretation of the experiments with the silica supported nickel-zinc oxide catalyst it was possible (in analogy with the previous results for the silica supported nickel oxide catalyst¹⁵) to summarize the results in the following way: Modifying the support with gamma rays, changing the technology of the catalyst and investigating the reaction kinetics with respect to both the former parameters, we were able to determine that the factors crucial for the catalyst activity are: first) the initial contact of the active-component intermediate with the support (precipitation deposition) and second) the time and temperature of the hydrogen interaction with the reduced catalyst during the final stage of catalyst preparation. Both these effects determine the energetic character of the formed nickel and hydrogen surface-structure and, in this way, also the resulting final activity.

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