
EFFECT OF GAMMA IRRADIATION OF SUPPORT ON THE ACTIVITY OF A HYDROGENATION NICKEL CATALYST

Rostislav KUDLÁČEK and Alena JUDLOVÁ

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

Received November 11th, 1982

The effect of previous gamma irradiation of support is studied for a hydrogenation nickel catalyst prepared by depositing the active component on kieselguhr; the rate and degree of calcination, degree of reduction, and surface area of the samples and the rates of heterogeneously catalyzed hydrogenations of maleic acid and sunflower oil are determined. The effect of the reduction temperature on the catalyst activity is examined in detail; due to interaction with hydrogen, two activity values are obtained for a given temperature.

Modification of catalyst or its support by ionizing radiation can affect the starting stage of the preparation, *viz.* the bonding of the active component to the support, and the activity of the final supported catalyst. Beta (from a ^{90}Sr — ^{90}Y source) or gamma (from a ^{60}Co source) irradiation of palladium supported on alumina resulted in a more than double increase in activity in the hydrogenation of aromatic unsaturated compounds^{1,2}. The activation energy remained unchanged by the irradiation, the frequency factor in the Arrhenius relation, however, increased. The authors^{1,2} suggest that the energy character of the reaction centres remained unaltered by the treatment, only their number is varied. The charging curves measured for the two types of catalyst as well as the thermodesorption of hydrogen point to different energies of bonding of hydrogen and different amounts of the latter on the catalyst surface. In a similar study for Pt-Pd and Rh catalysts on aluminium oxide³, a nearly double increase in activity was observed; the dependence of the reaction rate on the absorbed dose was also measured. The doses that are optimal from the points of view of activity and selectivity, respectively, are different. The irradiation of the catalyst results in an improved stability with respect to long-term heat stress. The effect of exposition of a final supported nickel catalyst to beta radiation was also studied⁴. The activity depended in a complex manner on the absorbed dose which induced changes also in the activation energy of the process.

Hydrogenation of maleic acid was used to investigate the effect of gamma irradiation from a ^{60}Co source on the activity of an industrial supported nickel catalyst⁵. Samples of carbonate origin were exposed to radiation after their drying and calcination, and the dependence of the reaction rate on the absorbed dose was measured for various temperatures of catalyst reduction. For 280°C, the rate decreased proportionally to increasing dose, for the region of 308—340°C, the reaction rates on the irradiated and unirradiated samples were comparable, and for 410 to 440°C, the reaction rate increased proportionally to the dose. The same model reaction was employed for the investigation of the effect of gamma irradiation on the properties of a nickel-zinc oxide supported catalyst⁶. Decisive for the activity was the first stage of the contact of the intermediate product of the active component with the support, hence, the precipitation deposition

process, and the temperature and time of interaction of the reduced catalyst with hydrogen in the final stage. The two effects determine the energy character of the formed surface structure of nickel with hydrogen and thereby the final activity of catalyst. The mechanism of formation of free radicals on the oxide surfaces on their prior irradiation and the effect of the radicals on the catalyst activity were also studied⁷.

In the present work the effect of ionizing radiation on the activity of a supported hydrogenation nickel catalyst is studied particularly *via* the dependence of the reaction rate on the catalyst reduction temperature.

EXPERIMENTAL

Samples of nickel catalyst supported on irradiated or unirradiated kieselguhr were prepared by the modified procedure⁸. Precipitated and boiled carbonate was repeatedly decanted and filtered and the suspension was dried at 130°C for 1 h, calcinated at 420°C for 30 min (ref.⁹), and reduced in a hydrogen stream directly in the reaction vessel accomodated in a tubular furnace. After cooling down, the vessel was transferred to the hydrogenation apparatus preventing deactivation of catalyst by oxygen gas. The support, untreated F2CH Borovany kieselguhr⁸, was exposed to ⁶⁰Co gamma radiation. Samples whose supports were exposed to the basic dose, a dose ten times as high, and a dose fifty times as high are labelled L7, L9, and L6, respectively, samples on unexposed support are labelled L1 and L2. The conditions of the hydrogenation of maleic acid and sunflower oil and the evaluation of the catalyst activity in the two reactions were as described previously^{8,9}. The calcination of the dry samples was followed on a Perkin-Elmer DSC-2 differential scanning calorimeter (heating rate 10°C/min over the region of 27–500°C, nitrogen atmosphere) and on a thermogravimetric apparatus under argon at 420°C (weighing accuracy ±0.1 mg). The reduction of the calcinated sample was monitored on the thermogravimetric apparatus in a hydrogen stream. The rate of hydrogen peroxide decomposition on the nonreduced sample was determined based on the amount of released oxygen.

RESULTS AND DISCUSSION

Our previous study⁶ of a nickel–zinc oxide catalyst deposited on kieselguhr revealed that the resulting activity of sample is affected by ionizing radiation more if the support has been exposed to radiation prior to the deposition of the active component than if the catalyst precursor is irradiated in some subsequent stage of preparation. A nickel catalyst supported on kieselguhr⁵ was found sensitive to irradiation after the calcination; with a suitable dose the activity increased as much as 35%. The investigations on nickel⁵ and nickel–zinc oxide⁶ catalysts also gave evidence that decisive for the sample activity are the temperature and duration of the final stage of preparation. When this dependence was compared for the modified and unmodified samples, the dose dependence was found to change in characteristic points. Thus, for establishing the effect of radiation on the support and ultimately on the final catalyst it is necessary to determine the dependence of activity on the temperature of the last stage of catalyst preparation, or to seek for the characteristic points of this dependence. The activity of a catalyst prepared on a technological scale was

observed¹⁰ to depend on temperature in a complex way. The drying or calcination procedures did not affect the catalyst activity appreciably, and therefore the conditions of these stages were held constant for all samples.

The dependence of the catalyst activity on the temperature of reduction was examined over the entire temperature region where the samples are active, *i.e.* 290 to 450°C in 4°C steps, for the irradiated sample L6 and the unirradiated samples L1 and L2. The reduction temperatures were measured with an error lower than 2%. The shape of the dependences was similar for all of the samples: the maximum activity was reached at two temperatures, whereas in the region between them the activity dropped appreciably. The temperatures of the maximum activity for samples L1, L2, and L6 were 358 and 400°C, 366 and 400°C, and 352 and 400°C, respectively. The difference between the degrees of hydrogenation in the maxima and minima was 15%, which is about five times more than the error of measurement.

For each sample, two activity values, whose difference exceeded considerably the error of measurement, were obtained at a given temperature of reduction. The dependence of activity on the reduction temperature was examined previously¹⁰ for a similar industrial supported nickel catalyst, and a curve exhibiting two maxima was obtained. Being regarded erroneous, the lower of the two activity values were not shown (the measurements were performed on a single sample). The experimental points in the present work could be fitted by a single curve, assuming that the differences were due merely to a scatter of results, or by two polynomials with the corresponding curves (Fig. 1). The correlation coefficient for the single curve was 0.6795, for the pair of curves, 0.9548 for the first curve and 0.9207 for the second.

The discussed dependence of the catalyst activity on the temperature of reduction and activation can be explained neither by surface inhomogeneity or nonuniform properties of the catalyst particles, nor by an incomplete degree of calcination and reduction. A feasible explanation lies in the interaction of the reducing hydrogen and nickel during the sample reduction. The thermodesorption spectra indicate the occurrence

TABLE I

Parameters in the Arrhenius relation: activation energy of hydrogenation of maleic acid E (kJ · mol⁻¹), frequency factor for hydrogenation of maleic acid A_{hyd} and frequency factor for decomposition of hydrogen peroxide A_{dec}

Sample	E	A_{hyd}	A_{dec}
L1	31.9 ± 6.3	$2.1 \cdot 10^7$	$4.25 \cdot 10^5$
L6	40.5 ± 9.3	$1.4 \cdot 10^9$	$8.35 \cdot 10^8$

of two characteristic hydrogen–nickel bonding structures of different energies forming during the sample reduction and cooling. These structures are decisive for the resulting catalyst activity and the dependence thereof on the temperature of preparation¹¹.

Sample L6, on irradiated support, exhibits a higher reaction rate than the unmodified samples with the same reduction temperature; or, it reaches the same reaction rate for a reduction temperature about 50°C lower (in the lower temperature region). This fact can be utilized also for the hydrogenation of unsaturated triglycides. The dependence of the reaction rate on temperature of the catalyst reduction was examined also for the hydrogenation of sunflower oil, and similar results were obtained as for maleic acid: on the irradiated sample the rate increased, the position of the maximum remaining unchanged, and two activity values were measured for a given temperature.

The dependences of the hydrogenation rates on the absorbed dose for the two substances are shown in Fig. 2. The degrees of conversion in the maximum of the first branch of the temperature dependence are plotted; the rates of the corresponding branches are in the same ratio.

For establishing the nature of the changes of the active centres induced by the support irradiation, the dependence of the hydrogenation rate on the hydrogenation

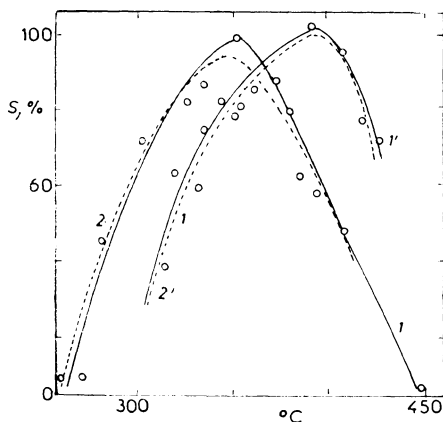


FIG. 1

Dependence of the degree of hydrogenation on the temperature of reduction for sample L6 1, 1' experimental values, 2, 2' regression curves

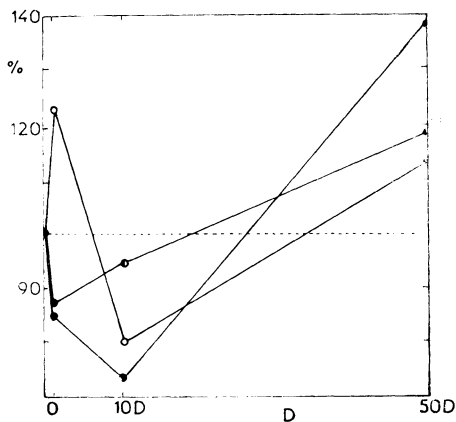


FIG. 2

Dependences of the degree of hydrogenation and surface area on the absorbed gamma dose (relative values with respect to the unmodified surface). ● Hydrogenation of maleic acid, ○ hydrogenation of sunflower oil; ● surface area

temperature (over the region of 9–28°C) was measured for samples L1 and L6. The activation energies of the two samples are identical within the experimental error, whereas the frequency factors differ by two order of magnitude (Table I). Hence, irradiation of support does not induce changes in the nature of the reaction centres, only their total amount is varied. Fig. 2 shows also changes in the surface area of the calcinated samples. The different shapes of this dependence for maleic acid and sunflower oil, for the lower absorbed dose, indicate that the radiation-induced changes do not manifest themselves to the same extent in the two reactions, similarly as has been observed for a nickel–zinc oxide catalyst⁶.

As a consequence of the increased surface area the degree of calcination of sample L6 also increased: the degrees of calcination for the unmodified and modified samples (under standard conditions) were 48.1% and 52.3%, respectively, the difference being higher than the error of thermogravimetric determination of the weight loss during the calcination. The differential calorimetry measurements gave evidence that the sample on irradiated support was calcinated faster. The thermogravimetrically measured degree of reduction of samples L1 and L6, on the other hand, was identical within the error of measurement. It can be inferred that in sample L6, with the support modified by radiation, more nickel is bonded to the surface than in sample L1 (the degree of precipitation of carbonate for the two samples, exhibiting identical nickel-to-kieselguhr ratios, was 100%, ref.⁸). This is consistent with the measurements of the catalytic decomposition of hydrogen peroxide taking place on the calcinated unreduced precursor (Table I).

The differences in the properties of catalyst on support exposed to ionizing radiation as compared with the unmodified catalyst can be ascribed to the induced changes in the support and the consequent affecting of the first stage of the catalyst preparation, *i.e.*, bonding of the nickel precipitate to the support.

The study of the kinetics of maleic acid and sunflower oil as well as the comparison of the samples on the radiation-treated and untreated samples indicates that decisive for the activity of the supported nickel catalyst are the first stage of its preparation, *i.e.*, the precipitation deposition process and the last stage, *i.e.*, the time and temperature of interaction of the reduced catalyst with hydrogen.

REFERENCES

1. Kuzembaev K. K., Sokolskii D. V., Tugelbaeva G. T.: *Izv. Akad. Nauk KazSSR, Ser. Khim.* 1980, 21.
2. Kuzembaev K. K., Tugelbaeva G. T.: *Tr. Inst. Org. Kat. Elkh. Akad. Nauk KazSSR* 20, 53 (1980).
3. Kuzembaev K. K., Sokolskii D. V.: *Sb. Soi Sov.-Jap. Konf. Katal.*, p. 164. Akad. Nauk KazSSR, Tashkent 1979.
4. Kuzembaev K. K.: *Zh. Fiz. Khim.* 54, 2359 (1980).
5. Kudláček R., Jelínková R.: *This Journal* 45, 1632 (1980).

6. Kudláček R., Solařová H.: *This Journal* 48, 2175 (1983).
7. Kazanskii V. B.: *Kinet. Katal.* 19, 279 (1978).
8. Kudláček R., Čmolík J.: *Prům. Potravin*, in press.
9. Kudláček R., Čmolík J.: *Chem. Prům.* 31, 127 (1981).
10. Kudláček R., Čmolík J.: *Chem. Prům.* 31, 472 (1981).
11. Kudláček R., Faltejsek J.: *Chem. Prům.*, in press.

Translated by P. Adámek.