EFFECT OF IONIZING RADIATION ON THE KINETICS OF HYDROGENATION ON THE Ni–MgO MIXED CATALYST

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The effect of gamma pre-irradiation of the mixed nickel–magnesium oxide catalyst on the kinetics of hydrogenation of maleic acid in the liquid phase has been studied. The changes of the hydrogenation rate are compared with the changes of the adsorbed amount of the acid and with the changes of the solution composition, activation energy, and absorbed dose of the ionizing radiation. From this comparison and from the interpretation of the experimental data it can be deduced that two types of centers can be distinguished on the surface of the catalyst under study, namely the sorption centres for the acid and hydrogen and the reaction centres.

The effect of ionizing radiation on the heterogeneous catalytic reactions is used for the elucidation of the mechanism of processes proceeding during the preparation of catalysts and during the reaction itself, as well as for the increase of the catalytic activity, selectivity, and for the increase of the yields of reactions of industrial interest. Sokolskii and coworkers[1] described the direct effect of beta and gamma radiation on the behaviour of the catalyst in the hydrogenation of benzene in the gas phase. The results show that the catalytic activity of the platinum/platinum black catalyst increases twice by the irradiation with beta particles of the energy of 0·76 MeV during the reaction; the effect of irradiation decreases with the increasing temperature and vanishes at 373 K. No change of the catalytic activity was observed if irradiated with gamma radiation. The effect of radiation on the nickel-catalyzed hydrogenation of nitrobenzene in isopropyl alcohol and on the platinum- and palladium-catalyzed hydrogenation of *p*-nitrotoluene in acetic acid was studied by Donald[2] (irradiation with X-rays of the energy of 1–2 MeV and with electrons of the energy of 2–3 MeV). The catalytic activity in all these cases increased. However, the activity increase of the nickel catalyst decreases with the increasing absorbed dose. The author assumes that at first the active centres are formed by the radiation and then they are destroyed by the same radiation. Sokolskii and coworkers[3], studying the amount of hydrogen adsorbed on the metals of the platinum group before and after irradiation with thermal neutrons found that the amount of hydrogen in these catalysts increases with irradiation. At the same time it was shown by the X-ray structural analysis that irradiation has no effect on the lattice parameters of the samples. However, the diameter of the catalyst particles diminishes nearly twice after irradiation so that — due to the increase of their surface — the amount of adsorbed hydrogen increases. Irradiation of the Raney nickel catalysts with fast neutrons (neutron flux $7 \cdot 10^{17}$ n cm^{-2}) increases the rate of acetone hydrogenation[4] by 30 per cent if the catalyst is treated at 393 K and 3·5 times if it is treated at 923 K (in this case, however, the absolute value of the reaction rate decreases several times). In the paper[4] the nature of the active centres, their disappearance during the thermal treatment, and their formation by irradiation is discussed.

Nickel–zinc oxide catalysts pre-irradiated with gamma radiation and neutrons[5], the same catalyst coated on silica and pre-irradiated with gamma radiation[6], and the deposited nickel catalyst[7] as well as the mechanism of surface processes during the hydrogenation of maleic acid were already studied in this laboratory.

This paper presents the results of similar studies of the changes of sorption and catalytic properties of Ni–MgO catalyst, modified by pre-irradiation with gamma rays.

EXPERIMENTAL

Preparation of catalysts with a variable content of nickel and magnesium, their treatment and composition, the hydrogenation apparatus, the experimental procedure, the measurements of the amount of oxygen adsorbed on the catalyst, and other details are given in the paper[8]. If not stated otherwise in the text, the following standard conditions were chosen for all measurements in this study, particularly in order to be certain that the reaction proceeded in the kinetic region: maleic acid concentration 0·1 mol l^{-1}, the total amount of the reaction solution 7 ml, the initial pressure of hydrogen 96·7 kPa, reaction temperature 297·5 K, temperature of the primary reduction 663 K, of the secondary reduction 563 K, the time of reduction and activation of the catalyst 80 min, the reaction vessel shaking rate 380 rpm, catalyst weight in the kinetic experiments 30 mg, in the sorption experiments 130 mg. Non-reduced samples of catalysts and samples re-oxidized on air at the room temperature after the primary reduction were irradiated in sealed glass ampoules using ^{60}Co source with the dose rate $1{\cdot}442 \,.\, 10^4$ Gy/h. No sample was radioactive after the irradiation. In the first series of experiments all samples with various ratios of nickel and magnesium oxide were irradiated with the dose of 1 MGy. In the second series the separately prepared sample containing 28 per cent of magnesium oxide was irradiated with doses of 10^5, $5 \,.\, 10^5$, 10^6, $1{\cdot}5 \,.\, 10^6$, and $3 \,.\, 10^6$ Gy.

The effect of pre-irradiation of the catalyst on the reaction rate was studied with samples of nickel–magnesium oxide catalysts in the series that differed in the modification step of the sample preparation. Because the reduced sample is pyroforic and must not be in contact with air before the reaction and because it is difficult to irradiate it in this state without changing its activity, the precursor was always irradiated. In the first series were irradiated samples after calcination, prior to the primary reduction and activation, *i.e.* the sample of mixed oxides.

In the second series every sample was reduced, cooled down in hydrogen, and then passivated by air at the room temperature. This means that irradiated were systems containing nickel with chemisorbed oxygen and the non-reduced magnesium oxide, the secondary reduction and activation of which preceded immediately the reaction. The change of the catalyst activity caused by its modification with gamma radiation was measured for two compositions of the reaction solution, particularly at pH 5·5 and 12, differing by the concentrations of individual dissociation forms of maleic acid and therefore also by the sorption behaviour of this organic substrate[9].

RESULTS AND DISCUSSION

Conditions necessary for the achievement of the sufficient and stable activity of the nickel–magnesium oxide catalyst and the dependence of the hydrogenation rate of maleic acid on the reaction parameters are described in the paper[8].

From the effect of radiation on the reaction rate and on the changes of acidity it follows (Fig. 1) that the reaction mechanism evidently changes with the change of the catalyst composition. The change appears at 20–25 mol. % of magnesium oxide in the catalyst. At lower contents of magnesium oxide the reaction rate on the irradiated catalyst is higher, the sorption of the acid is low, and there is no difference in the amount of adsorbed acid between the irradiated and non-irradiated samples. The reaction rate on samples with a higher content of magnesium oxide is lower after irradiation and at the same time these samples adsorb a markedly lower amount of the organic substance. The changes of the reaction rate and of the adsorbed amount of the acid are the same and it can be therefore assumed that they are in correlation in this concentration range of magnesium oxide. However,

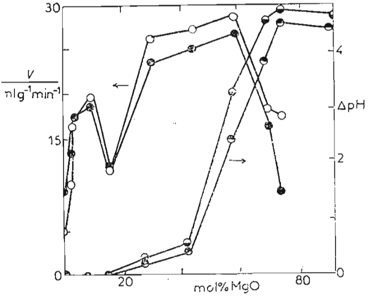

FIG. 1

Effect of irradiation on the hydrogenation rate and on the acidity changes for various compositions of the catalyst. Primary reduction: pH 5·5; reaction rate: ● irradiated sample, ○ non-irradiated sample; changes of acidity: ◓ irradiated sample, ◒ non-irradiated sample

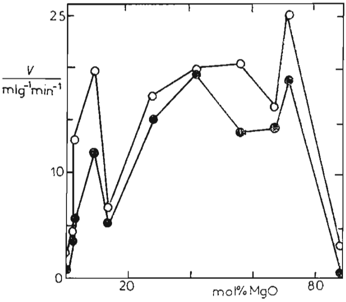

FIG. 2

Effect of irradiation on the hydrogenation rate for various compositions of the catalyst. Primary reduction; pH 12: ● irradiated sample, ○ non-irradiated sample this correlation was not found for the solution of pH 12 (Fig. 2) and for the sample after secondary reduction (Fig. 3). The change in the character of sorption as well as the inversion of the irradiation effect take place in the sample with 16·1 mol.% of magnesium oxide, which exhibits a remarkably lower rate than the nearest samples in the series (similarly as it is shown in Fig. 1). Moreover, the reaction rate change due to irradiation is the lowest on the catalyst of this composition.

It can be assumed that in this region of the catalyst composition the interaction of both components and their participation on the catalytic activity changes qualitatively. However, monotonous structural changes with the increasing concentration of MgO have been found in all samples by the X-ray structural analysis[10]. The comparison of these two measurements – *i.e.*, of the effect of radiation on the reaction rate and of the X-ray structural analysis – indicates that defects connected with the change of the sample composition without any effect on the structural parameters are formed during the modification of the solid catalyst with the ionizing radiation.

Changes of the solution acidity, directly related to the amount of adsorbed acid, vary with the composition of the catalyst in the same extent for both primary and secondary reductions (Figs 1 and 3). Similarly as in the case of the nickel–zinc oxide mixed catalyst[9] it can be assumed that maleic acid is preferentially adsorbed on magnesium oxide. However, the dependence of the hydrogenation rate on the composition of the catalyst has not a monotonous character (Figs 2 and 3). Using the mentioned analogy, this effect can probably be explained by the assumption that the sorption of hydrogen increases in the opposite direction, *i.e.*, with the increasing content of nickel in the sample. The resulting change of the reaction rate in dependence on the composition of the catalyst is then given by the adsorbed amount of individual reaction components and by the changes of the ability of the catalyst

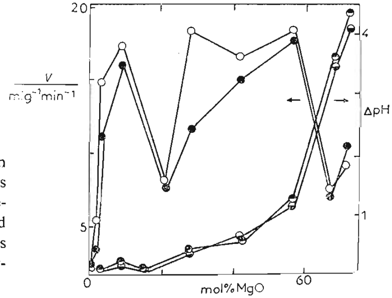

FIG. 3

Effect of irradiation on the hydrogenation rate and on the acidity changes for various compositions of the catalyst. Secondary reduction; pH 5·5; reaction rate: ● irradiated sample, ○ non-irradiated sample; changes of acidity: ◓ irradiated sample, ◒ non-irradiated sample to add hydrogen on the double bond, depending on the varying ratio of the adsorption and reaction centres.

Pre-irradiation of the catalyst with gamma radiation changes the reaction rate and this change is markedly dependent on the absorbed dose of gamma radiation (Fig. 4). At low doses the hydrogenation rate decreases substantially after irradiation of the mixed catalyst as well as after irradiation of the reduced sample with chemisorbed oxygen. The reaction rate increases with the increasing dose and becomes greater than the rate on the non-modified sample. In the dose range under study this increase by irradiation amounts to 12 and 16%, respectively, with a distinct maximum in the case of the primary reduction. The interpretation of this dependence is difficult because radiation modifies only the precursor, it does not affect the sorption and reaction centres themselves but only the conditions of their subsequent formation. From Table I and Fig. 4 it is evident that the rate change due to pre-irradiation cannot be related to the changes of the amount of the adsorbed organic component which is always higher for the irradiated sample. The amount of the adsorbed hydrogen and the change of reaction centres are evidently more important.

The comparison of the temperature dependences of the reaction rate on the irradiated and non-irradiated catalysts (Fig. 5) can solve the problem of the changes of the bond strength of the substrate with the catalyst surface due to its modification by radiation. These dependences for the sample with 67·3 mol.% of MgO (irradiated by the dose of 10^6 Gy) render the value of the activation energy $E_a = 45 \cdot 6 \pm$

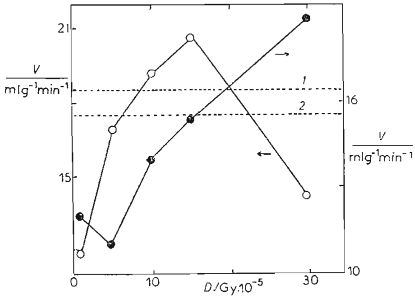

FIG. 4

Reaction rate as a function of the absorbed dose of gamma radiation. ○ Primary reduction; *1* non-irradiated sample; ● secondary reduction, *2* non-irradiated sample; content of magnesium oxide 28·2 mol.%

± 5·4 kJ/mol for the non-irradiated sample and $E'_a = 62 \cdot 3 \pm 10 \cdot 5$ kJ/mol for the irradiated sample. The irradiation changes also the pre-exponential factor in the Arrhenius equation, which depends on the number of reaction centres: $A = 1 \cdot 88 \,.\, 10^{10}$ for the non-irradiated sample, and $A' = 1 \cdot 89 \,.\, 10^{12}$ for the irradiated sample. Fig. 5 shows that the lines for the irradiated and non-irradiated samples are not parallel and that they intersect. From the measured dependences and their comparison three reaction temperature regions of different character can be distinguished: in the region governed by the addition of hydrogen on the double bond the irradiated sample gives a lower rate at lower temperature, at higher temperature its rate is higher, and after the turning point when sorption becomes the rate-determining process, the irradiated samples give lower rates.

For the interpretation of the effect of pre-irradiation of the nickel–magnesium oxide catalyst it can be assumed that on the catalysts under study there are different centres on the surface for the sorption of the organic substance and for hydro-

TABLE I

Comparison of the adsorbed amount of maleic acid on the irradiated and non-irradiated samples

Adsorbed dose, Gy . 10^5	0	1	5	10	15	30
Primary reduction	0·051	—	0·118	0·061	—	0·477
Secondary reduction	0·049	0·069	0·095	—	0·063	0·060

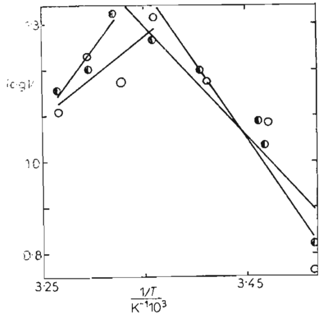

FIG. 5

Reaction rate as a function of reaction temperature. ○ irradiated sample, ◐ non-irradiated sample; content of magnesium oxide 67·2 mol.%

gen, and that there are centres on which proceeds the reaction. The pre-irradiation of samples changes preferentially the process of reduction and activation of the catalyst reduced by hydrogen.

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