HYDROGENATION OF MALEIC ACID ON NICKEL–MAGNESIUM OXIDE MIXED CATALYSTS AND THE ISOTOPE EFFECT OF SOLVENT

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The activity of nickel–magnesium oxide mixed catalyst in liquid phase hydrogenation was investigated in dependence on the composition of the solid phase and on the preparation procedure. The isotope effect of substitution of light water by heavy water, the kinetic dependences, and the sorbed amount of the reacting maleic acid were examined with a view to deducing the reaction mechanism.

Catalysts constituted by two components usually exhibit higher catalytic activity than as would correspond to a mere addition of the two components[1]. The mutual influencing of the components appears also in the non-additive nature of the sorption of the reacting substrates, degree of reduction, formation of active centres, their resistance to heat treatment of the catalyst and their activation. These observations were made previously for nickel oxide–zinc oxide mixed systems in model reaction of hydrogenation of maleic acid[2]; the effect of replacing light water as the solvent by heavy water on the kinetics of the hydrogenation and on the sorption behaviour of the reacting substances was also studied.

In the present work, the properties were studied of an analogous mixed nickel catalyst in which the second component was magnesium oxide; samples with various proportions of the two components were prepared. The topics studied were the conditions of sample preparation for attaining a steady activity, dependence of the activity on the primary and secondary reduction temperatures, the relation between the sorbed amount of the acid and the reaction rate, the isotope effect of the solvent, and the concentration dependence.

EXPERIMENTAL

The apparatus for measuring the reaction rate, the working procedure, the pH measurements, the solution preparation, and other experimental parameters have been described previously[2]; the way of handling heavy water solutions and of examining the isotope effect of the solvent have been given in the work[3]. The reduced catalyst sample after cooling in hydrogen is transferred to the measuring apparatus, which then is filled with hydrogen and solution of maleic acid in water; these operations have to be accomplished preventing access of air. The following experimental conditions were applied unless stated otherwise: shaking speed 380 r.p.m. hydrogen pressure 97·3 kPa, temperature 25°C, 7 ml of 0·1M maleic acid solution, catalyst reduction period 80 min. The amount of maleic acid sorbed on the catalyst was measured as described in[3]. The catalyst for sorption was prepared in the same manner as for the reaction and handled in the same manner as at the beginning of the reaction, for identical conditions to be ensured for the sorption and the reaction. The amount of the acid sorbed on the catalyst, in gram per gram catalyst, is calculated tby using the formula $a = y(1 - z)/G$, where y is the amount of the acid in the solution before the sorption (g), z is the height ratio of the polarographic waves corresponding to the concentrations before and after the sorption, and G is the catalyst weight before the reduction (g).

The series of catalysts with different nickel-to-magnesium ratios was prepared by mixing calculated volumes of 1M solutions of nickel nitrate and magnesium nitrate, and precipitation with 15% excess of 1M solution of potassium carbonate. The precipitate was filtered out, decanted with distilled and tridistilled water until negative reaction for nitrates, and dried at room temperature for a day and, subsequently, at 125°C for 3 h. The calcination of the sample was carried out at 500°C on air for 6 h. The composition of the samples as given in Table I was determined chelatometrically[4]. Table I gives also the degree of reduction of the mixed oxides, α, defined as the ratio of the sample weights after and before the reduction. The method used for the evaluation of the α value did not allow values below 5% to be determined, which was the case with samples No 7 and higher. For a series of experiments, sample No 6A was prepared with composition identical with that of sample No 6.

The reaction rate and error of measurement were evaluated from the time course of the hydrogen uptake (difference between the levels of the manometer connecting the measuring and the

TABLE I

Composition of the catalysts and degree of reduction at 380°C

Sample No	NiO content mol.%	MgO content mol.%	Degree of reduction[a] %
1	100	0	96
2	98·0	2·0	97
3	97·1	2·9	69
4	90·1	9·1	16
5	83·9	16·1	9
6	71·7	28·2	7
7	54·9	42·1	[b]
8	43·4	56·6	[b]
9	32·6	67·2	[b]
10	28·2	71·8	[b]
11	10·2	89·8	[b]
12	1·4	98·6	[b]
13	0	100	[b]

[a] Error of determination of the degree of reduction is 5%; [b] degree of reduction below 5%.

reference parts of the apparatus), using the least squares method in linear regression. The error of measurement of the reaction rate did not exceed 2%.

RESULTS AND DISCUSSION

For an examination of the dependences of the reaction rate on various parameters, the conditions must be ensured such that the reaction proceeds in the kinetic region, with exclusion of external transport. In the experimental conditions used, the limiting rate of hydrogen transport from the gas phase to the catalyst surface was found to be 12 mm/min (Fig. 1); this value of the pressure drop in the connecting manometer represents the uptake of 0·54 ml H_2/min. In all experiments the catalyst weight was chosen so that this value was not surpassed. The maximum rate of hydrogen uptake in an integral static reactor can be regarded as a convenient auxiliary criterion in a particular case for establishing the region suitable for conducting the reaction.

The nonreduced mixed oxides do not exhibit a measurable catalytic activity, as demonstrated by the measurements with the samples No 5 and No 11. The dependence of the reaction rate on the catalyst composition (Fig. 1, curve *1*) is markedly nonmonotonic, displaying a maximum. The degree of reduction, *i.e.* the number

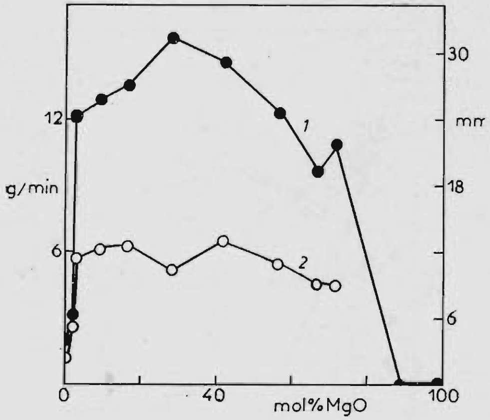

FIG. 1

Dependence of the rate of hydrogenation of maleic acid on the composition of the catalyst. Reduction: 350°C, 80 min, pH 5·7, catalyst weight approximately 70 mg; *1* reaction rate per unit weight of the catalyst; *2* rate of hydrogen uptake expressed by the difference of the manometer levels

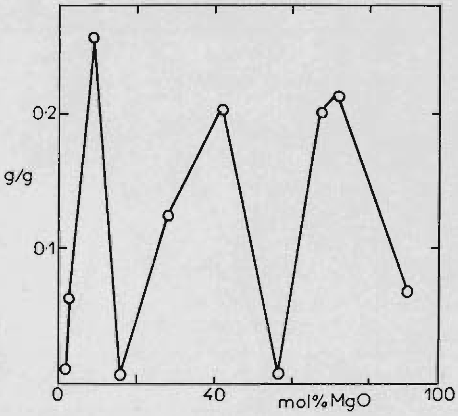

FIG. 2

Dependence of the sorbed amount of maleic acid on the catalyst composition of reduced atoms of nickel (magnesium oxide does not reduce in the conditions applied[4]), varies with the sample composition, but the values do not correlate with the reaction rates. Although this comparison is not decisive, because more important to the catalyst activity is the surface concentration of the reduced nickel, it can be deduced (particularly from the data of the samples No 1 and No 4) that the number of the reduced atoms is not a unique factor governing the reaction rate. The sorbed amount of one of the reactants, maleic acid, also varies nonmonotonically, but the shape of its dependence on the sample composition is different from that of the reaction rate (Fig. 2); thus the sorbed amount of the acid is not the factor exclusively

TABLE II

Dependence of the reaction rate on the reduction temperature for sample No 6. Reduction period 80 min

Temperature, °C	495	470	445	395	360	330
Rate, ml/g min	11·5	24·5	22·2	21·0	15·6	0

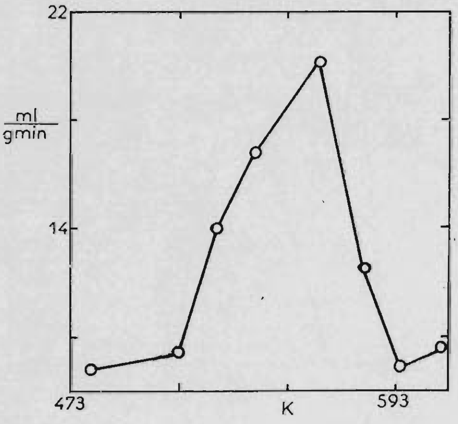

FIG. 3

Dependence of the reaction rate on the temperature of secondary reduction. Primary reduction 390°C, 80 min; secondary reduction 80 min; sample No 6A

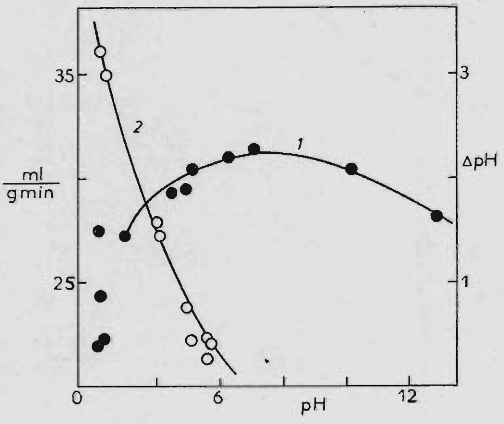

FIG. 4

Dependence of the reaction rate and change in the pH of the solution on its composition. Sample No 6; reduction: 380°C, 80 min; pH for the starting solution, ΔpH — difference between the initial value and the value after the reaction governing the reaction rate, either. Thus it is the interaction of hydrogen with the sample that seems to be the most significant factor controlling the catalyst activity. As found by Pospíšil[4], the reduction proceeds predominantly within the several first minutes, after 10 – 12 min the mass loss of the reduced sample does not change any more, the degree of reduction remains contant. On the other hand, the time necessary for the steady catalytic activity to establish is multiply longer – in the case in question, steady catalysts could only be prepared by 80 min reduction in hydrogen. The dependence of the reaction rate on the temperature of reduction for primary reduction of the sample No 6 is given in Table II; the dependence on the temperature of secondary reduction (the sample reduced primarily at 360°C is allowed to cool down in hydrogen and re-oxidized freely on air) for sample of the same composition, 6A, is shown in Fig. 3.

The character of the two dependences and comparison of the corresponding maxima can be interpreted as follows. There are two competitive processes that can take place during the primary and secondary reduction heat treatment. The reduction gives rise to active centres, which, however, at the same time are thermally broken down. During the secondary reduction, additional new centres may be created. It is not reasonable to assume that the samples after the primary and secondary reduction should be different to such an extent that the maxima of the rates and, hence, the thermal character of the processes should be thermally so different. Another interpretation is based on an analogy with nickel carrier catalyst[5], where study of the isotope effect of hydrogenation and deuteration and of prior gamma irradiation indicated that it is activation of the reduced catalyst by hydrogen that affects appreciably the catalyst activity and nature of the active centres. The two maxima of the reaction rate, at 290°C for secondary reduction and at 370°C for primary reduction, agree with the dependence of the reaction rate on the reduction temperature for calcinated and reduced samples of the applied nickel. It can be thus assumed that decisive in the catalyst activity is the interaction of hydrogen, the magnitude of the activity being determined by the temperature of that interaction, hence by the energy of the bonding of hydrogen in the active centre.

The minimum temperature of primary reduction sufficient for attaining a steady catalytic activity of sample, 360°C, is higher than in the case of nickel–zinc oxide catalysts[2], 270°C, whereas the minimum temperatures of secondary reduction are virtually equal (160 – 170°C), for comparable reduction periods in both cases. For a nickel carrier catalyst, the same temperature has been also found for hydrogenation of benzene[6], and for the same catalyst type, for hydrogenation of maleic acid[5].

Maleic acid in aqueous solutions dissociates to the first and the second degrees. The concentrations of the various dissociation species depend upon the solution pH, the ions being differently sorbed on the catalyst surface[3]. In the case of nickel–magnesium oxide catalysts, there is no pronounced difference in the sorption of the non-dissociated and the two dissociated species, as follows from the dependence of the reaction rate on the pH of the solution for the sample No 6 (Fig. 4); and analogous result was obtained also for the sample No 7. In both cases, an inexpressive maximum of the reaction rate occurs at pH 7 to 8, where the concentrations of the HA^- and A^{2-} ions of the acid are equal. In view of the fact that the dependence of the reaction rate on the pH is not analogous to that of the concentrations of either ion on the pH (ref.[2]), it can be concluded that the sorption of maleic acid on nickel–magnesium oxide catalysts is essentially different from the previously examined sorption and reaction of the acid on nickel–zinc oxide catalysts[2]. For both samples, the reaction rates for a maleic acid solution not adjusted with sodium hydroxide (pH 1·7) are irreproducible and the time dependence of the hydrogen uptake is not linear, as in such acidic solution catalyst breakdown and dissolution takes place. The dependence of the reaction rate on the composition of the solution (Fig. 4) refers to the initial pH of the solution before the sorption of the acid on the catalyst. If the reaction rate is related to the pH of the solution after the sorption at the beginning of the reaction, no unique monotonic function is obtained; this indicates that obviously the predominating reactant is that part of the acid that on contact of the solution with the catalyst is sorbed at the very beginning of the reaction.

In order to examine the relation between the sorbed amount of maleic acid and the reaction rate, the isotope effect of the solvent was measured for the reaction kinetics as well as the sorbed amount of the acid (Figs 5 and 6, respectively). An inverse isotope effect of the solvent was found; the kinetic isotope effect is also given by the

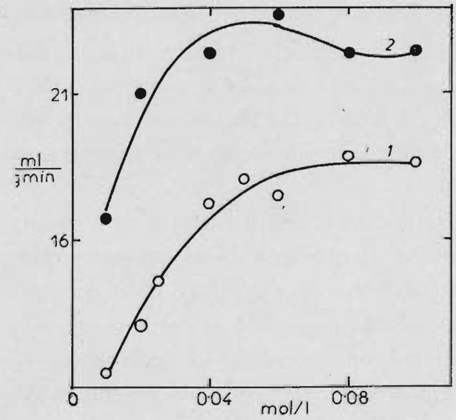

FIG. 5

Dependence of the reaction rate on the concentration of maleic acid and isotope effect of the solvent. 1 Light water, 2 heavy water

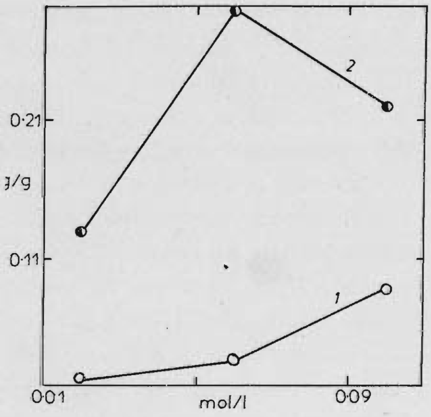

FIG. 6

Dependence of the sorbed amount of the acid on its concentration and isotope effect of the solvent. 1 Light water, 2 heavy water

TABLE III

Dependence of the change in the solution pH on the initial concentration of maleic acid and the isotope effect of the solvent in its sorption

Concentration mol/l	ΔpH^a		Isotope effect[b]
	H_2O	D_2O	
0·02	0·7	1·2	0·58
0·06	0·4	0·7	0·57
0·1	0	0·1	—

[a] Difference in the solution pH value before and after the sorption; [b] the $\Delta pH_{H_2O}/\Delta pH_{D_2O}$ ratio.

TABLE IV

Reproducibility of the rate of the reaction in heavy water

Concentration mol/l	Arithmetic mean ml/g min	Maximum deviation ml/g min	Error %
0·06	23·62	0·19	1·4
0·1	22·3	0·10	0·66

The difference in the reaction rate for the two concentrations is 5·8%.

TABLR V

Isotope effect in substitution of light water by heavy water

Parameter	Light water	Heavy water	Isotope effect
Initial amount, 10^{-4} mol	1·6	1·6	—
Adsorbed amount, 10^{-5} mol	1·6	4·8	0·33
Reacted amount, 10^{-4} mol	1·04	1·2	0·86

inverse isotope effect of the sorbed amount of the acid. As Fig. 5 demonstrates, the dependence of the reaction rate on the concentration of the solution is anomalous and is of the same nature as that of the sorbed amount of maleic acid on the initial concentration (Fig. 6; here only the points corresponding to the extremum of the reaction rate were measured); it should be noted that the differences in the reaction rate exceed significantly the statistically evaluated error in reproducibility (see the case of triplicate measurements in Table IV). The different change in the pH due to sorption (Table III) can be partly explained by the different solvent effect of light and heavy water, because in the two solvents the concentrations of the various dissociation species vary. Apart from the sorbed amount being considerably larger in the case of heavy water, there is also a difference in the concentrations of the organic substance at which the saturation is attained in the adsorption isotherm. This is borne out also by the value of the change in the pH of the solution brought by the sorption at the beginning of the reaction. The above-mentioned experiments with light water using concentration of the acid 0·1 mol/l thus were carried out in the region where the sorbed amount of the acid was independent of its concentration (saturated state of the sorption isotherm). For an accurate determination of the concentration dependence and its interpretation, the sorption isotherm must be known in the conditions of the reaction and of its beginning. From these dependences it is also possible to choose in advance the concentration region in which the concentration dependence does or does not appear.

The sorbed and reacted amounts of maleic acid in the two solvents are mutually compared in Table V. The acid concentration during the reaction obviously does not affect directly the reaction rate, the latter is thus only governed by the initial concentration and the related initial sorbed amount of the reactant. This accounts then for the fact that the reaction is zero order with respect to maleic acid, as the reaction rate virtually does not vary until the end of the reaction. This equilibrium and final state are affected by the isotopic substitution of the solvent – 75% maleic acid reacted in heavy water and 65% in light water. In a heterogeneous system, the dependence of the reaction rate on the concentration of the reactant and the order of the reaction are thus to be evaluated in different ways. Different dependences can be obtained for the initial concentration parameter and for the concentration during the reaction; this takes place particularly in case that the course of the reaction is not affected directly by them, and the sorption–desorption equilibrium is affected both by the product and the solvent. Isotopic substitution of the solvent can conveniently facilitate a more detailed study of such relations, as the experiments performed demonstrate.

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