

ISOTOPIC SOLVENT EFFECT IN HYDROGENATION ON A SUPPORTED NICKEL CATALYST

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A supported nickel catalyst, commonly applied in industrial hydrogenation of fats and oils, was used to study the effect of replacement of the light water solvent, with heavy water, on the addition of hydrogen on a double bond of maleic acid. The effect was investigated of the composition and temperature of the solution, on the reaction rate, as well as, the relation between the reaction rate and the amount of the acid adsorbed on the catalyst. Reaction mechanism with respect to the hydrogenated organic compound is proposed.

In order to study the mechanism of the heterogeneously catalyzed hydrogenation one needs to know the reaction between the organic compound and the catalyst surface, and the way, in which the reaction course is affected by the form of the organic compound in the solution. This purpose can be accomplished by means of the isotopic solvent exchange — using heavy water instead of light water. The resulting isotopic solvent effect in the hydrogenation kinetic can lead to measurable changes in some of the reaction stages, influencing *e.g.*: *a*) the character of sorption of the organic compound molecules and ions and the degree of catalyst surface coverage, *b*) the dissociation equilibrium of the hydrogenated acid, *c*) the hydrogen solubility in the solvent and the sorption of hydrogen on the catalyst, *d*) the isotopic composition of the gas phase resulting from the isotopic exchange H_2-D_2O on the catalyst.

Earlier studies of the isotopic solvent effect in maleic acid hydrogenation, using nickel-zinc oxide type¹ and nickel-magnesium oxide type² mixed catalysts have shown that in the studied water-dihydric acid system, the above changes are observed. If zinc oxide is present in the catalyst, the first dissociation form of the acid HA^- is preferentially sorbed on the catalyst and this sorption determines the reaction rate. If magnesium oxide is present, the reaction course is independent on the change of the dissociation form of the acid but the sorption of the organic compound again determines the reaction course. In both cases it has been found that organic substrate is with preference sorbed on the zinc oxide and magnesium oxide microzones and the reaction itself is of zero order with respect to this reactant. It has been also observed that only that amount of the compound which was adsorbed in the initial stage of reacting, takes part in the reaction itself, determining thus the final degree of hydrogenation.

These results, which were obtained predominantly by comparison of the hydrogenation kinetics in the light water and heavy water solvents, justified application of the above technique for studying the relation between the reaction organic compound and the supported nickel catalyst.

EXPERIMENTAL

Nickel, supported on silica, was prepared in the laboratory from a nickel(II) chloride solution, obtained by dissolving the already used industrial catalyst. The subsequent preparation steps followed the technology described in paper³. After decanting and filtering the precipitate, the sample was dried at 130°C for 30 minutes, calcinated at 420°C in the air for 30 minutes and reduced at 415°C for 50 minutes. The course of the reaction itself was measured using the apparatus and procedure described earlier³. The solutions were prepared from tridistilled water with a natural deuterium content and heavy water of equal purity with a 99.6 mol% deuterium content, respectively. Isotopic dilution of heavy water, caused by the contact with air humidity during its manipulation and by addition of H^+ ions from the acid and OH^- ions from the base (when fitting pH of the solution) remained less than 1 mol%. Unless stated otherwise, the following conditions were selected to ensure that the reaction proceeded in the kinetic region: the volume of solution 7 ml, the reaction temperature 25°C, the agitation frequency 380 c/min, the hydrogen pressure 97 kPa, the time during which the reaction was measured 15 minutes. The catalyst sample and the solution for the sorption measurement were prepared in a way identical with the beginning of the hydrogenation. Yet, the agitation frequency was slower and the hydrogenation degree was in this case negligible. After three minutes of sorption the catalyst suspension was removed by centrifugation. The maleic acid concentration in the solution, before and after the sorption, was determined polarographically using a phosphate buffer with pH 7.8 (ref.²). Since for the polarographic measurements, the maleic acid solution has to be diluted twenty five times, no isotopic solvent effect is observed. The reaction rate was evaluated from the linear part of the hydrogen-consumption time-dependence, applying least squares analysis. The obtained hydrogenation degree was evaluated from the ratio of the amount of hydrogen consumed and the theoretical hydrogen consumption — given by the amount of the acid in the reacting solution.

RESULTS AND DISCUSSION

The dependence of the reaction rate on the time of reduction of the catalyst has shown that within the 30–80 minutes range, the reaction rate changes only slightly. The reduction time 50 minutes was selected for all measurements.

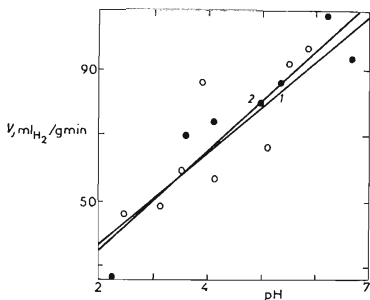


FIG. 1

Dependence of the reaction rate on pH of the initial maleic acid solution for 1 light water 2 heavy water; acid concentration 0.15 mol/l

For given reaction conditions, the hydrogen consumption rate increased proportionally with the catalyst weight, up to 17 mg. With higher catalyst amounts, the consumption of hydrogen remained constant. Catalyst amounts 7–8 mg were selected for the subsequent experiments, to ensure that the rate limiting step was given by the reaction on the catalyst surface itself. The reaction rate, related to a unit catalyst amount, increases in this reaction region slightly with the increasing value of the catalyst weight, in a linear way. Since the maximum attainable hydrogenation degree also increases in the studied range of catalyst weights (it reaches 77% for 7 mg of the catalyst, 100% for 17 mg) it is possible to assume, for constant volume of the solution, that the catalyst becomes poisoned. The composition of the maleic acid solution does not change with the changing amount of the catalyst, as it was the case of hydrogenation on the oxide catalyst^{1,2}.

In the pH range 2.2–6.2, the reaction rate increases linearly with the increasing pH (Fig. 1). This course does not depend on the concentration changes of the dissociated form of maleic acid, for both solvents. Within the measured range of changes of the acidity of the solution, the concentration of these dissociation forms significantly varies and the concentration of the first dissociation step HA^- passes through a distinct maximum. This maximum appears for ordinary water at pH 3.9 and for heavy water at pH 4.4 (ref.¹). Since, within the error of measurement, no difference in the reaction rate was observed when substituting light water with heavy water, one can conclude that the form in which the organic acid exists in the solution has no effect on the hydrogenation kinetics. At both boundary values of the studied pH range of the solution, we have measured the reaction-rate dependence on temperature, for the light water solvent. The apparent activation energies obtained from Arrhenius equation are for pH 2.9, $E_1 = 41.8 \pm 8 \text{ kJ/mol}$ and for pH 6.3, $E_2 = 52.2 \pm$

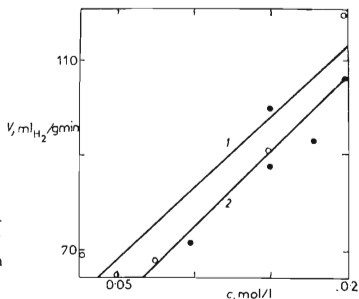


FIG. 2

Dependence of the reaction rate on concentration of the maleic acid solution for 1 light water 2 heavy water; pH of solution 5.1–5.5

± 4 kJ/mol. The corresponding frequency factors equal $A_1 = 4.8 \cdot 10^{10}$ and $A_2 = 5.9 \cdot 10^{10}$, respectively. The obtained values suggest that the character and the number of the surface sites varies only very little with the changing composition of the solution.

An information on the character of the maleic acid sorption, at the beginning and in the course of the reaction, can be obtained from a way in which the solution pH is changing after the catalyst has been contacted with the solution of the acid. This change was measured for the previously studied mixed catalysts and it has been observed that it depends on the initial composition of the solution and on the content of the oxide in the catalyst. Within the error of measurement, no pH shift was found with the presently studied nickel catalyst, for various initial pH values of the solution and different concentrations of the acid. In the same sense, no difference was observed between the light water and the heavy water solvent.

Under identical conditions – with respect to the preparation of the catalyst, the solution and the gas phase at the onset of hydrogenation, we have determined polarographically the maleic acid concentration change, before and after the catalyst was contacted with the solution. No adsorption on the surface was detected for any value of the pH, concentration of the solution and catalyst weight. Similarly, no difference was observed in behaviour of the light water and the heavy water solvent.

The reaction rate dependence on the maleic acid concentration in the solution (Fig. 2) evidences that the reaction is evidently first order with respect to the concentration of the organic substrate. This result is in agreement with the generally accepted mechanism of catalyzed reaction in which the organic compound is sorbed very weakly and in small amounts or not at all⁴. Analogical character of this dependence obtained with the light water and heavy water solvent again shows that neither the form in which the acid exists in the solution nor the equilibrium between the acid and the surface of the catalyst affect the hydrogenation mechanism.

Comparison of the relations between the organic compound and the studied silica supported nickel catalyst, on one hand, and the organic compound and nickel–zinc oxide (respectively nickel–magnesium oxide) catalyst, on the other hand, supports the earlier derived conclusions according to which hydrogen is sorbed preferentially on the nickel atoms at the catalyst surface while the acid is sorbed mostly on the micro-zones of the oxide. Since the hydrogenation selectivity is, evidently, connected with the sorption ratio of the organic compound and hydrogen on the surface of the catalyst⁵, it is reasonable to assume that the observed differences between the studied types of catalysts can be connected with the above property.

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