EFFECT OF IRRADIATION AND OF REPLACEMENT OF HYDROGEN BY DEUTERIUM ON THE KINETICS OF HYDROGENATION OF MALEIC ACID ON A NICKEL CATALYST

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Liquid phase hydrogenation reaction was studied on modifying the solid catalyst by preliminary irradiation and replacing the reacting hydrogen by deuterium; the changes in the reaction rate were measured and the phenomena on the catalyst surface, particularly the change in the catalyst activity, were investigated. For the model reaction, the dependences of the reaction rate on the temperature of reduction and of the successive activation of the catalyst on the absorbed gamma dose were followed, and the dependences of the reaction rate on the reaction temperature were compared for the hydrogenation and deuteration. Isotope effect was found in the influence of the reacting medium on the catalyst property. The activity of the nickel carrier catalyst is governed by its interaction with hydrogen after the reduction, particularly by the temperature of this process.

In radiation catalysis, the radiation can act upon the reacting system either from an external source or from a radionuclide incorporated in the solid phase. In both cases, radiation-chemical transformations may occur in addition to the catalyzed reaction examined, and the process requires some safety measures. For this reason, it is more convenient to irradiate the catalyst preliminarily during its preparation, and to study then the changes in the reaction kinetics[1]. The effect of prior irradiation of a arrie catalyst on its activity for liquid phase hydrogenation has been extensively studied by Sokolskii and his fellow workers. The subject of their investigations was catalysts of the platinum group elements on which model hydrogenation reactions were performed. Prior irradiation of osmium black and platinum dioxide in a nuclear reactor brought about a threefold enlargement of their surface and an adequate 2-2·5-fold rise of the reaction rate[2]. Neutron or alpha irradiation of platinum and palladium dioxides led to an increase of the reaction rate, 1·6—2 times in the latter case, in dependence on the solvent used; this has been explained in terms of an increase in the surface dispersity[3]. The changes in the ability of platinum, osmium, and palladium catalysts and their mixed samples to sorb hydrogen, resulting from their irradiation in a nuclear reactor, were studied on the case of hydrogenation of dimethylethinylcarbinol[4]. A copper catalyst prior irradiated by accelerated electrons exhibited a higher activity if the dose was $3 . 10^4$ J kg^{-1}; when X rays were applied, the activity doubled[5] with the dose 10^4 J kg^{-1}. The activity of a nickel catalyst for hydrogenation of acetone increased three times on irradiation by neutrons[6], the effect, however, was lower if the catalyst had been heated.

Catalyzed reactions of unsaturated organic substance with deuterium can be employed for preparation of labelled compounds as well as for study of the hydrogenation mechanism. In both cases, the addition of deuterium to the catalyst and substitution of the former for the hydrogen atoms of the organic molecule have to be taken into account[7-9]. The mechanism of hydrogenation of fatty acid esters on platinum, palladium, and nickel catalysts has been studied with regard to their interaction with the calalyst and with hydrogen (or deuterium), geometric and positional isomerization, and behaviour of the conjugated bonds on the catalyst[10-13]. No differences were observed between the hydrogenation and deuteration or tritium addition rates, and it has been concluded that decisive for the reaction rate is the solubility of hydrogen or deuterium. Hirota[14] studied the process of deuteration of cyclic ketones and the way in which their molecules are bound to nickel catalyst. An analogous study with deuterium for hydrogenation of methylcyclohexanone on platinum catalyst has been done by Teratoni[15], who also has examined the accompanying hydrogen–deuterium exchange reaction. For a nickel-zinc oxide mixed catalyst, a mechanism of hydrogenation of maleic acid has been suggested based on investigation of the kinetic isotope effect on replacing hydrogen by deuterium[16], the diffusion of the reacting gas over the catalyst surface being assumed to be the limiting stage.

On a commercial coated nickel catalyst, it is convenient to examine the dependences of the reaction rate and mechanism of hydrogenation on a model reaction of hydrogen addition to the double bond of maleic acid[17]. These phenomena can be also used for investigation of the isotope effect of prior irradiation on the reaction rate and activity of the catalyst.

EXPERIMENTAL

The hydrogenation was performed on industrial catalysts supplied after drying as "hydrocarbonate from filter press" or after calcination in a rotary furnace as "hydrocarbonate from calcining furnace". The solutions were prepared from maleic acid and sodium hydroxide, both reagent grade purity, and triply distilled water. Electrolytic hydrogen from a pressure cylinder was used for the reduction, reduction calcination, and activation; hydrogen and deuterium for the reaction were obtained electrolytically in a laboratory apparatus and freed from oxygen on a desoxo catalyst. The reductions, reduction calcinations, and activations with hydrogen were conducted in a reaction vessel heated by a tube furnace immediately before the experiment, preventing access of air. In the hydrogenation apparatus, the hydrogen uptake was measured by monitoring pressure changes[18-20]. The reaction conditions used were as in[17]. Unless stated otherwise, the parameters were as follows: reaction temperature 25°C, solution volume 7 ml, acid concentration 0.1 $\text{mol}\,l^{-1}$, shaking speed 380 rpm, hydrogen pressure 97 kPa. The samples were irradiated from a ^{60}Co source.

RESULTS AND DISCUSSION

The catalyst samples were irradiated applying various gamma doses and designated as follows:

Dose, Gy	0	10^4	10^5	10^6
Hydrocarbonate from calcining furnace	A	B	C	
Hydrocarbonate from filter press	E	F	G	H

The samples A, B, and C were examined in dependence on the primary reduction temperature in the region of 280–470°C using the reduction period of 90 min (Fig. 1). The dependence of the reaction rate exhibits periodical variations of the activity, with extremes. Differences between the reaction rates on untreated and radiation-treated samples are apparent particularly at higher reduction temperatures. The dependence of the reaction rate on the absorbed dose is different for different reduction temperatures, its character changes within the temperature region examined: At the lowest temperature, the rate decreases with increasing dose; at 308°C and 340°C, the dependence displays an extremum for the dose of 10^4 Gy; at a higher temperature, 380°C, the rate is independent of the dose; at 410°C and 440°C, the reaction rate increases proportionally to the dose; and at the highest temperature, 470°C, the activity of the unirradiated sample and the sample irradiated by the dose of 10^5 Gy is the same, whereas that of the sample irradiated by the dose of 10^4 Gy is lower. The reaction rate is more dependent on the temperature of reduction in the case of irradiated samples than in the case of unirradated ones.

In the case of the hydrocarbonate from calcining furnace, the character of the dependence of the catalyst activity on the dose or temperature is not very expressive, obviously because the sample consists of a mixture of calcinated and uncalcinated agglomerates[17]. The effect of prior irradiation was therefore studied analogously on an uncalcinated – and thus more homogeneous – intermediate product, from

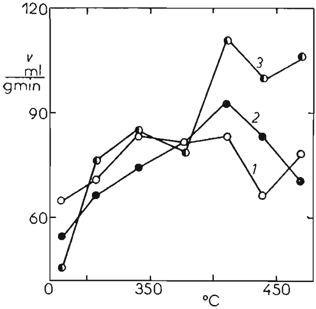

FIG. 1

Dependence of the Reaction Rate on the Temperature of Reduction and Dose of the Absorbed Gamma Radiation

Catalyst: hydrocarbonate from calcining furnace; sample: *1* A, *2* B, *3* C.

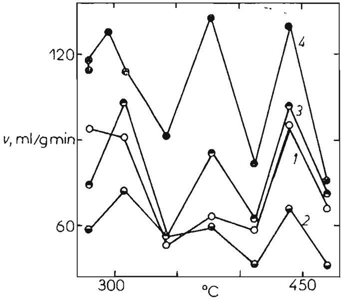

FIG. 2

Dependence of the Reaction Rate on the Temperature of Reduction Calcination and Absorbed Dose of Gamma Radiation

Catalyst: hydrocarbonate from filter press; sample: *1* F, *2* H, *3* G, *4* E.

which the final catalyst could be prepared by reduction calcination[17]. The results for the applied doses of 10^4, 10^5, and 10^6 Gy in the same region of heat treatment in hydrogen (Fig. 2) have a more expressive nonmonotonic character. Again, the irradiated samples show the same character of dependence of the reaction rate as the unirradiated sample, but the rate is lower in all cases. The positions of the extremes in the dependences of the reaction kinetics on the heat treatment temperature for the two catalyst intermediate products mutually correspond, they are, however, opposite in character – they are "phase shifted". It can be thus concluded that the catalysts prepared in the two different ways are different. From the technological point of view it is also of importance that the rate on the hydrocarbonate from filter press is up to 30% higher and, at the same time, a lower heat treatment temperature is required – at 300°C the activity of the catalyst is twice as high as that of the hydrocarbonate from calcining furnace.

The nonmonotonic shape of the dependence of the reaction rate on the temperature of the reduction calcination for this intermediate product is not fortuitous, it follows from the nature of the interaction between hydrogen and the catalyst and its dependence on the temperature, which is evidenced by a comparison of the irradiated and unirradiated samples, particularly by the dependences of the reaction rate on the dose and on the temperature of the reduction calcination. The irradiated samples are less active than the unirradiated ones, the dependences being different for different doses. For a low temperature, 280°C, the dependence on the dose is decreasing; as the temperature increases, the reaction rate for the dose of 10^5 Gy becomes higher against the two other doses; for the highest temperatures, the values for 10^4 and 10^5 Gy are the same,whereas for the dose of 10^6 Gy the activity is lower.

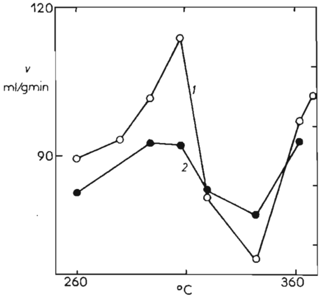

FIG. 3

Dependence of the Reaction Rate on the Temperature of Reduction Calcination

For *1* hydrogenation, *2* deuteration Catalyst: hydrocarbonate from filter press.

Thus changes in the character of the dose dependence appear again at reduction calcination temperatures corresponding to the extreme values of the reaction rate. This can be explained so that on the reaction centres prepared at different temperatures, the effect of the prior irradiation and its intensity appear differently.

For a detailed study of the interaction of hydrogen with the catalyst, the hydrogenation and deuteration on the unirradiated hydrocarbonate from filter press – sample E – were compared (Fig. 3). A pronounced isotope effect and its inversion were found in the temperature region examined. The highest differences between the hydrogenation and deuteration rates appear for the reduction calcination temperature corresponding to the extremum of the reaction rate (Table I). The deuteration rate can be higher in case that the limiting stage of the reaction is the breakdown of the double bond in the hydrogenating molecule of hydrogen or deuterium, as deuterium exhibits a lower energy of atomic bond. A lower deuteration rate can occur in case that the decisive phenomenon is surface diffusion or a process controlled by the molecular weight. These limiting stages cannot be supposed to change on increasing the temperature of the catalyst preparation by 25–30°C, from the temperature of the maximum reaction rate, 308°C, to that of the minimum, 342°C. The discussed change in the reaction rate dependence can be explained so that after the contact with deuterium of the catalyst reduced in hydrogen, the hydrogen in the catalyst is replaced by deuterium before the filling with the solution of maleic acid. A different energy of bonding of hydrogen and deuterium can be thus assumed in the structure of the activated catalyst. This is borne out by the dependence of the

TABLE I

Dependence of the Isotope Effect on the Temperature of Reduction Calcination

t °C	v^H	v^D	v^H/v^D
260	88·8	82·4	1·08
280	93·1	–	–
294	101·6	92·6	1·10
308	113·7	92·2	1·23
320	81·5	83	0·98
342	67·9	78·4	0·88
362	97	93	1·04
378	100·3	–	–

reaction rate on the reaction temperature for the minimum in the dependence of the reaction rate on the reduction calcination temperature. For the catalyst preparation temperature 342°C and period 90 min, the apparent activation energies for the reacting hydrogen and deuterium were found to be $E^{H} = 48{\cdot}4 \pm 6{\cdot}4$ kJ mol^{-1} and $E^{D} = 32{\cdot}1 \pm 2{\cdot}4$ kJ mol^{-1}, respectively, in the region of reaction temperatures 9·5 – 33·5°C. This change in the character of the active centres and the associated change in the catalyst activity, brought about by the replacement of hydrogen by deuterium, is a new phenomenon, which has to be taken into account when the possible causes of the changes in the kinetics of hydrogenation and deuteration catalyzed by a solid are analyzed. As follows from the experiments, the catalyst is markedly affected by the medium and the influence involves also the isotope effect.

Summing up the experimental data, the activation of a hydrogenation nickel catalyst can be explained as follows. Interaction of hydrogen with the reduced catalyst leads to the formation of a nickel structure such that hydrogen can be bound to the surface and activated for subsequent addition to the double bond. The interaction of hydrogen and the catalyst after the reduction is thus significant for the activation of the catalyst. Hydrogen is not bonded by sorption forces only, as after the reduction and the subsequent activation during the cooling, the sample "remembers" the activation temperature, and the hydrogen and the nickel structure on the catalyst surface are not affected by the sorption–desorption equilibrium and its shift on the cooling from the temperature of reduction and activation down to room temperature.

REFERENCES

1. Kudláček R., Cabicar J.: This Journal *43*, 838 (1978).
2. Sokolskii D. V., Nadykto B. T., Pak A. M., Ten E. I., Kuznetsov J. D., Rozmanova L. D.: Khim. Vys. Energ. *5*, 74 (1971); Dep. VINITI N° 2061 – 70.
3. Sokolskii D. V., Pak A. M., Nadykto B. T., Rozmanova L. D., Korolev A. V., Chursin G. M.: Khim. Vys. Energ. *5*, 356 (1971); Dep. VINITI No 2840 – 71, 3222 – 71.
4. Sokolskii D. V., Pak A. M., Ten E. I., Nadykto B. T.: Vestn. Akad. Nauk KazSSR *1971*, 24; *Katalicheskie Reaktsii v Zhidkoi Faze*, p. 277. Alma Ata 1972.
5. Seaman J.: U.S. 3 803 010, 9. 4. 1974.
6. Tomio J.: J. Chem. Soc. Jap., Pure Chem. Sect. *91*, 86 (1970).
7. Frankopol M.: Isotop. Radiat. Technol. *9*, 447 (1972).
8. Burwell R. L. jr: Catal. Rev. *7*, 25 (1972).
9. Taylor T. I. in the book: *Catalysis* (J. Emmet, Ed.), Vol. V, p. 257. Reinhold Publ. Co, New York 1957.
10. Bitner E. D., Selke E., Rohwedder K. K., Dutton H. J.: J. Amer. Oil Chem. Soc. *41*, 1 (1964).
11. Rohwedder W. K., Bitner E. D., Peters H. M., Dutton H. J.: J. Amer. Oil Chem. Soc. *41*, 33 (1964).
12. Koritala S., Selke E.: J. Amer. Oil Chem. Soc. *48*, 222 (1971).
13. Koritala S., Scholfield C. R., Selke E., Dutton H. J.: J. Amer. Oil Chem. Soc. *50*, 11 (1973).
14. Hirota K., Touroude R., Miysaka M., Matsumura Ch.: J. Res. Inst. Catal. Hokkaido Univ. *25*, 37 (1977).

15. Teratani S., Tanaka K., Ogawa H., Taya K.: J. Catal. *51*, 372 (1978).
16. Kudláček R., Cabicar J.: This Journal *43*, 1826 (1978).
17. Kudláček R., Čmolík J.: Chem. Prům., in press.
18. Kudláček R., Cabicar J.: This Journal *43*, 1818 (1978).
19. Kudláček R., Solařová H.: This Journal, in press.
20. Kudláček R., Lokoč J.: This Journal, in press.

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