

KINETICS OF REDUCTION OF NICKEL(II) OXIDE WITH DEUTERIUM

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Reduction of nickel(II) oxide with hydrogen and deuterium has been followed in the temperature interval 240–440°C. In the range of lower temperatures and in the initial stage of the reaction an inversion isotopic effect takes place which changes, with increasing degree of reduction and with increasing temperature, into a normal isotopic effect. The kinetics of reduction both with hydrogen and with deuterium can be quantitatively described by two different relations, according to the degree of reduction. The values of the apparent activation energy and the changes in the kinetics of reduction, when catalyzed by addition of Pd, in dependence on the reducing medium, allow to estimate the conditions under which the rate-determining step are the internal transport processes. The isotopic effect, characterizing the region of high reduction degree and the region of higher temperatures, is due to diffusion, either of molecular hydrogen, or, in the presence of a catalyst, of the activated hydrogen, to the reaction interface.

The importance of the nickel catalyst was the reason, why a great deal of attention has been paid to the reduction of nickel(II) oxide with hydrogen^{1,2}. Several authors have demonstrated the catalytic effect of metals of the Pt-group³ and of salts^{4,5}, either as mechanical admixtures or impregnated on the NiO surface, on its reduction. Also the preliminary treatment of the oxide by some gases⁶ leads to an increase in the velocity of nickel nucleation and to an acceleration of the reduction.

Up to now, the reduction of metal oxides with deuterium has been studied only sporadically. Richard⁷ investigated the isotopic effect in the reduction of copper(I) oxide with a mixture of ¹²CO–¹⁴CO, particularly from the point of view of experimental technique. The participation of water vapour in the transport processes in the low-temperature catalytic reduction of tungsten oxide was proved⁸ by means of the mixtures H₂/H₂O, D₂/D₂O, H₂/D₂O and D₂/H₂O. In all the above-mentioned cases the isotopic effect was found.

The present study is aimed at following the differences in the kinetics of reduction of nickel(II) oxide with hydrogen and deuterium.

EXPERIMENTAL

Nickel(II) oxide was prepared by calcination of the basic carbonate, prepared by precipitating the solution of nickel(II) nitrate by the solution of potassium carbonate in 15% excess with

respect to stoichiometry. Concentration of the solutions was 1 mol/l, the chemicals were of reagent grade purity. After drying at 20°C for 24 h and at 120°C for 3 h the precipitate was calcinated on air for 4 h at 400°C. For experiments the fraction of the grain size in the interval 0.05–0.1 mm was selected by sieving. Specific surface area of the oxide, measured by adsorption of nitrogen at low temperatures, was 41.4 m²/g. According to the results of analysis the preparation contained 99.40 weight% of nickel(II) oxide.

The kinetics of reduction was studied thermogravimetrically in the temperature interval 240–440°C, using the apparatus, described in paper⁹. Deuterium was obtained by electrolysis of the solution of (D) potassium hydroxide, prepared from heavy water of the USSR provenience (purity 99.8% D₂O) and metallic sodium. With sample weights 50 mg and at flow rate of hydrogen or deuterium 56 ml/min the rate and the time course of the reduction do not depend on these parameters.

RESULTS

In the region of lower reduction temperatures (240–290°C) the inversion isotopic effect can be observed, which is manifested by the higher rate of reduction of nickel oxides with deuterium as compared to the reduction with hydrogen under identical experimental conditions. From Fig. 1 as well as from further results it is evident that the reduction with deuterium proceeds at a rather higher rate only in the initial and intermediate stages of the reaction in dependence on temperature. In the region of high degree of reduction the oxide is reduced with deuterium at a lower rate than with hydrogen. At higher reduction temperatures (320–440°C) the inversion isotopic effect changes into a weak normal isotopic effect and the reduction with deuterium is slower (Fig. 2) over the whole range of the reduction degree. The duration

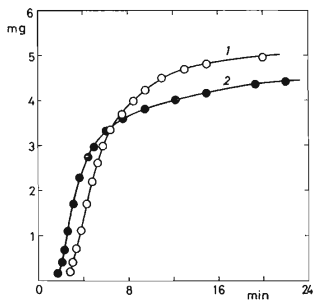


FIG. 1

Time Courses of the Reduction of NiO with Hydrogen and Deuterium at 240°C
1 H₂; 2 D₂.

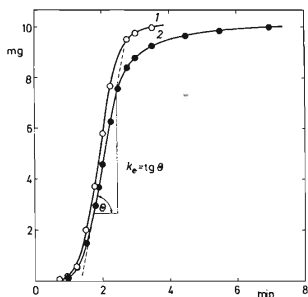


FIG. 2

Time Courses of the Reduction of NiO with Hydrogen and Deuterium at 320°C
1 H₂; 2 D₂.

of the induction period is practically unaffected by the reduction medium used.

The value of both normal and inversion isotopic effect is, in the temperature interval examined, practically independent of temperature (Table I). The isotopic effect (IE) is defined as the ratio of empirical rate constants $IE = k_{e(H_2)}/k_{e(D_2)}$. For $IE < 1$ it is the inversion effect, for $IE > 1$ the normal isotopic effect. The empirical rate constants (k_e) were determined using the method according to Delmon¹⁰ and were read off from the basic curves of the time course of reduction, as it can be seen from Fig. 2.

From the figures it can be further seen that the reduction isotherms of nickel(II) oxide by both hydrogen and deuterium follow a sigmoid path, which is characteristic of autocatalytic decomposition processes¹ of solid substances. The reduction kinetics can be quantitatively described, regardless of the reducing gas, by the relation $\alpha^{1/2} = kt$, where α denotes the degree of reduction in time t and k is a constant. The equation is valid for initial, or also intermediate values of α up to $\alpha \approx 0.5$ in dependence on temperature. In the region of intermediate reduction degree of the sample at lower temperatures and in the region of fading out of the reaction the kinetics of the reduction is quantitatively described by equation $1 - \alpha = e^{-kt}$, where the symbols have their usual meaning. The rate constants of the reaction, k , were therefore evaluated as the slopes of the linear intercepts of the function $\alpha^{1/2} = f(t)$ for the initial stage and of the function $\log(1 - \alpha) = f(t)$ for the regions of intermediate

TABLE I

Values of the Isotopic Effect at Different Reduction Temperatures $a_{IE} = k_{e(H_2)}/k_{e(D_2)}$

Temperature °C	240	260	290	320	350	380	410	440
a_{IE}	0.73	0.73	0.61	1.33	1.01	1.10	1.07	1.09

TABLE II

Values of the Apparent Activation Energy (kJ/mol) of the Reduction of NiO with Hydrogen and Deuterium for Different Degrees of Reduction, α

Gas	$\alpha \approx 0.0-0.3$	$\alpha \approx 0.5-1.0$	
		440-320°C	320-240°C
H ₂	84.99	34.66	93.13
D ₂	61.13	26.37	70.34

and high values of α . The values of apparent activation energy of reduction were calculated from the temperature dependence of the rate constants in Arrhenius coordinates (Table II) and in the region of higher values of α two values of activation energy were read off, corresponding to two intervals of reduction temperatures: (440–320°C) and (320–240°C). In all cases the reduction with deuterium proceeds with a lower activation energy as compared to the reduction with hydrogen.

Also the effect of partial pressure of hydrogen and deuterium on the time course of reduction was studied. The sample was reduced with a mixture nitrogen–hydrogen (deuterium) at constant flow rate 56 ml/min and temperature 290°C. In the region of low partial pressures up to $p_{\text{H}_2} = 72.53$ kPa and $p_{\text{D}_2} = 56.26$ kPa the reduction rate increases linearly with partial pressure of both gases. At higher than the above mentioned values the reaction rate becomes independent of partial pressure.

The standard-weight sample was further reduced at 290°C with 0.5% Pd asbestos added, which was triturated with nickel(II) oxide in an agate mortar to form a homogeneous mechanical mixture. The addition of the catalyst leads (Fig. 3) to a significant increase in the rate of reduction with hydrogen over the whole range of α (value of the ratio $k_{e(\text{cata})}/k_e = 1.69$). A similar, but quantitatively lower effect was observed in the reduction with deuterium ($k_{e(\text{cata})}/k_e = 1.50$).

DISCUSSION

As follows from experimental results, the reduction of nickel(II) oxide with hydrogen and deuterium proceeds as a typical autocatalytic reaction. The kinetics of reduction can be expressed, in dependence on the degree of reduction, by the same equation, irrespective of the reducing medium. The initial stage of the reaction, when the formation of metallic nuclei takes place in the surface layers, can be described ac-

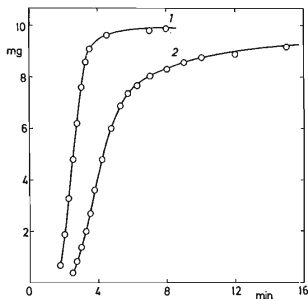


FIG. 3

Time Courses of the Reduction of NiO with Hydrogen at 290°C and of the Same Sample Reduced under the Same Conditions in the Presence of 0.5% Pd Catalyst

1 With catalyst, 2 without catalyst.

according to the theory¹⁰, assuming a constant nucleation velocity, by the relation $\alpha^{1/n} = kt$, where $n = 2-3$, according to the geometry of the nuclei. The validity of this equation, which was experimentally confirmed by other authors^{10,11}, is supported also by our results. The final phase of the reduction of nickel(II) oxide can be quantitatively described, according to different models of solid substances decomposition^{2,11}, and this even in the case of an oxide without carrier. The probable reason is the varying distribution and size of particles, caused by the way of preparation or by the preliminary treatment of the sample before the reaction.

In the absence of the catalyst the reduction with molecular hydrogen proceeds as a donor reaction in which the transfer of electrons from the sorbed hydrogen into the solid phase and the formation of metallic nuclei are the rate-determining steps in the initial stage of the reaction. From the studies of the effect of partial pressure and flow rate of the reducing gas it follows that under the given experimental conditions the initial reaction rate in the range of lower temperatures is not influenced by diffusion of hydrogen or deuterium molecules from the gaseous phase towards the surface of the catalyst. Thus it can be supposed that the isotopic effect, characterizing this stage of the reaction, is connected with the rate and with further conditions of the establishing of dynamic equilibrium on the surface of the reduced oxide. Since the binding energies of both isotopes to the surface are different, the surface will be filled up differently by H_2 or D_2 molecules and the degree of coverage for the same surface will differ for the two isotopes. It follows from both theoretical and experimental works that under otherwise identical conditions the heavier isotope is sorbed in greater amounts^{12,13}. Thus the reduction with deuterium can be started simultaneously from a greater number of centers or from energetically differing centers. This is also supported by the finding that the reaction with deuterium proceeds with a lower activation energy (Table II), *i.e.*, different kinds of surface centers are probably operative with respect to the higher isotope from which the reduction is initiated. The resulting initial reaction rate is higher in comparison with that of the reduction with hydrogen. With increasing reduction temperature an increase of the total effect of transport processes can be assumed, and that even in the initial stage of the reaction. From kinetic studies of hydrogen and deuterium sorption on various catalysts it is known¹⁴ that the values of the ratio of adsorption rate constants k_{H_2}/k_{D_2} lie close to the value of the ratio $(m_{H_2}/m_{D_2})^{-1/2}$, where m is the mass of the molecule. From this relation it follows that the normal isotopic effect is operative in processes governed by molecular diffusion, owing to the higher velocity of diffusion of molecules of the lighter isotope. Consequently, with increasing reduction temperature a continuous change of the inversion effect to normal isotopic effect may be expected, which is also in accordance with the experimental results.

The relatively low values of activation energy of reduction in the intermediate and final phases of the reaction in the region of higher temperatures (Table II) are

also an evidence of the determining effect of diffusion processes. In these phases the reduction takes place inside the individual nuclei and the growing layer of the new metallic phase slows down the transport of gas molecules towards the active reaction interface. The value of activation energy of the reduction with hydrogen at lower temperatures is in very good agreement with the literature data² and allows to assume that under these conditions the reaction proceeds in the kinetic region. In the case of reduction with deuterium the effect of diffusion cannot be excluded even in this region. Moreover, the reaction may be retarded by diffusion of the gaseous product (D_2O).

Recently, a great deal of attention has been devoted to the study of transport processes in the reduction of metallic oxides with hydrogen in connection with the catalytic effect of admixtures, especially of metals of the platinum group¹⁵. Most authors assume the dissociative adsorption of hydrogen on the catalyst accompanied by ionization¹⁶ and diffusion of the activated hydrogen to the surface of reduced oxide, or through the layer of nonreduced carrier, or eventually by direct diffusion between the individual grains of the oxide (the so-called "jump-over" and "spill-over" effects). Also other mechanisms of activation were proposed¹⁷.

If the activation of hydrogen molecules takes place at the surface of the microheterogeneous admixture, then the sites of its contact with the oxide can serve directly as centers of nucleation and of growth of the nuclei of metallic phase. The effect of catalytic admixtures is thus manifested by the shortening of the induction period (Fig. 3). The mentioned concepts of the mechanism of activation are in full accordance with our experimental results. If the cleavage of the bond in hydrogen or deuterium molecule and the reaction of free atoms takes place in the presence of a Pd catalyst, a normal isotope effect may be expected, with respect to the higher value of the dissociation energy in the D_2 molecule. Catalyzed reduction with hydrogen will proceed at a higher rate than a similar reaction with deuterium, which was also experimentally proved. The increase of the catalytic effect of admixtures in the presence of water, preadsorbed on the oxide surface, is explained by some authors¹⁶ by the acceleration of diffusion of active hydrogen, probably in the form of hydroxonium ion, through the water layer. At medium and high degrees of reduction of the sample a metastable, practically monomolecular water layer can be always assumed to be present which is immediately desorbed into the gaseous phase. In the absence of catalyst this water inhibits the reduction. In the case that it accelerates, in the presence of the catalyst, the diffusion of active intermediates (H_3O^+ , D_3O^+), we can, with respect to the higher mass of D_3O^+ , expect lower diffusion velocity of these ions. Consequently, the catalyzed reduction with deuterium will proceed more slowly than the analogous reaction with hydrogen even at higher values of α , where the determining effect of diffusion is very probable. This conclusion is also in agreement with experimental results.

REFERENCES

1. Frety R., Tournayan L., Charcosset H.: *Ann. Chim. (Paris)* 9, 341 (1974).
2. Verhoeven W., Delmon B.: *Bull. Soc. Chim. Fr.* 10, 3065 (1966).
3. Nowak E. J., Koros R. M.: *J. Catal.* 7, 50 (1967).
4. Roman A., Delmon B.: *C. R. Acad. Sci., Ser. C* 273, 94 (1971).
5. Charcosset H., Frety R., Soldat A., Trambouze Y.: *J. Catal.* 22, 204 (1971).
6. Charcosset H., Frety R., Labbe G., Trambouze Y.: *J. Catal.* 35, 92 (1974).
7. Richard J.: *Thesis*. University of Lyon, Saclay 1962.
8. Boudart M., Vannice M. A., Benson J. E.: *Z. Phys. Chem. (Frankfurt am Main)* 64, 171 (1969).
9. Pospíšil M., Cabicar J., Rejholec V.: *This Journal* 35, 1319 (1970).
10. Delmon B.: *Introduction à la Cinétique Hétérogène*, p. 197. Technip, Paris 1969.
11. Arora B. R., Banerjee R. K., Mandal N. K., Ganguli N. G., Sen S. P.: *Technology* 10, 193 (1973).
12. Maxted E. D., Moon Ch. H.: *J. Chem. Soc.* 1936, 1542.
13. Krumbiegel P.: *Isotopieeffekte*, p. 72. Akademie Verlag, Berlin 1970.
14. Geib K. H. im Buche: *Handbuch der Katalyse* (G. M. Schwab, Ed.) Vol. 6, p. 36. Springer, Wien 1943.
15. Charcosset H., Delmon B.: *Ind. Chim. Belge* 38, 481 (1973).
16. Ilchenko N. I.: *Usp. Khim.* 41, 84 (1972).
17. Benson J. E., Kohn H. W., Boudart M.: *J. Catal.* 5, 307 (1966).

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