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Carrier and Water Vapor Effects in the Reduction of $\text{NiO}-\gamma\text{Al}_2\text{O}_3$ System

Wpływ nośnika i pary wodnej na redukowalność katalizatorów $\text{NiO}-\gamma\text{Al}_2\text{O}_3$

It has been known for a long time now that supported nickel oxide reveals a considerably lower reactivity when compared with non-supported nickel oxide. The reduction of supported nickel oxide with hydrogen requires much higher temperatures and even then a large number of nickel ions most often remain unreduced. Still greater difficulties and stronger inhibition of supported nickel oxide reduction occur with the presence of water vapor in hydrogen [1-4]. In the literature these phenomena are reported as connected with very high dispersion of supported nickel oxide [2-5]. It is thought that small NiO crystallites on a carrier are hard to react with hydrogen or even that reduction is impossible [2-5]. It is supposed [2, 4] that with the coexistence of large and small crystallites in the system NiO -carrier (SiO_2 , Al_2O_3 etc.) the former should be reduced more easily (sooner and quicker) than small crystallites. This effect of the dispersion of supported nickel oxide on its reducibility is further deepened by water vapor which does not allow the reduction of NiO crystallites larger than it is possible with dry hydrogen [2, 3]. However, the literature does not give an exhaustive answer to question of why small nickel oxide crystallites on a carrier are harder to reduce and why the size of unreducible NiO crystallites increases in the presence of water vapor. In our earlier paper [2] we suggested the following reasons:

- i) strong influence of diffusion factors which make the reduction of small NiO crystallites, placed deep in the carrier's micropores, more difficult,
- ii) the reaction of NiO with the carrier, more effective with small rather than large crystallites, which yields unreducible or hardly reducible compounds,
- iii) strong stabilization of small NiO crystallites by the carrier and its surface hydroxyl groups.

In the present paper we intend to report the experimental data concerning the scope of the inhibitory effect of water vapor at various reduction temperatures and to discuss in greater detail the hypotheses proposed previously.

EXPERIMENTAL

The studies were carried out on $\text{NiO}-\gamma\text{Al}_2\text{O}_3$ system obtained by coprecipitation of nickel and aluminium hydroxides from the solution of their nitrates by means of ammonium hydroxide at 343 K and pH 7. The precipitate was dried and ground to power and then 3×5 mm pellets were formed. After calcination at 673 K for 10 hours the system contained 58.0 wt. % NiO . The total surface area was $218 \text{ m}^2/\text{g}$ and the mean size of NiO crystallites — 8.6 nm.

The reduction of supported nickel oxide was carried out at atmospheric pressure in a flow system for six hours with dry and wet hydrogen. Hydrogen was dried by means of silica gel, 5 A molecular sieves and liquid nitrogen trap. Wet hydrogen reduction was carried out at a constant partial pressure of water vapor of 26.7 hPa, obtained by the saturation of dry gas with lightly boiling water which was followed by dropping off water vapor excess in a thermostat cooler. The reduction degree was determined by the gravimetric method. The mean sizes of nickel oxide and nickel were determined by the method of X-ray line broadening employing the CuK_α radiation and, as a reference, MgO crystallites larger than 100 nm. The area of total surface was obtained by the BET method on the basis of argon adsorption at 78 K, assuming that one argon atom covers the area of 0.157 nm^2 .

RESULTS

The water vapor effect on the values of the reduction degrees of nickel oxide supported on $\gamma\text{Al}_2\text{O}_3$, obtained at various temperatures, is presented in Fig. 1. The inhibitory action of water is seen within the whole range of the temperatures examined and is particularly strong at lower temperatures — at 773 K the reduction degree is decreased only by 5%, while at 623–673 K already by 20%.

The determinations of the mean size of nickel crystallites and unreduced nickel oxide (Fig. 2) have revealed the expected [2, 3] increase in their dimensions after the introduction of water vapor into hydrogen. One may also see that larger nickel oxide crystallites remain unreduced at lower temperatures than at higher temperatures. At the same time, there occur similar changes in the mean size of nickel crystallites being formed. The latter dependences are valid for both dry and wet hydrogen.

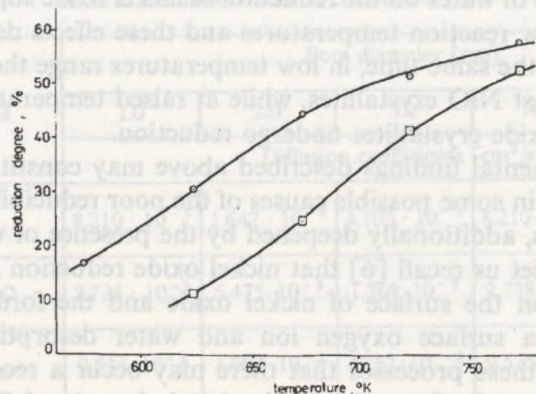


Fig. 1. The effect of reduction temperature and partial pressure of water vapor on the degree of reduction (\odot — $p_{H_2O} = 0$ hPa, \square — $p_{H_2O} = 26.7$ hPa)

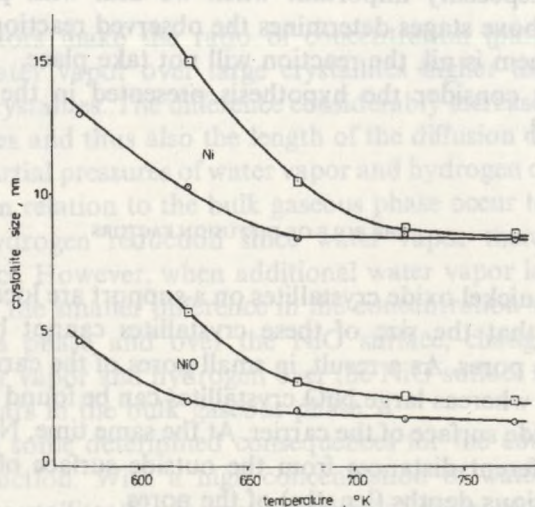


Fig. 2. The dependence of the mean size of nickel and unreduced nickel oxide crystallites on reduction temperature (\odot — $p_{H_2O} = 0$ hPa, \square — $p_{H_2O} = 26.7$ hPa)

DISCUSSION

From the literature [1, 2] it is known that even very small amounts of water vapor in hydrogen cause high percentage changes in the reduction degree and sizes of NiO crystallites undergoing reduction to the metal. With larger amounts of water vapor these changes gradually become moderate. The strongest

inhibitory action of water on the reduction of nickel oxide supported by $\gamma\text{Al}_2\text{O}_3$ is revealed at low reaction temperatures and these effects decrease with rising temperature. At the same time, in low temperatures range the reduction occurs only in the largest NiO crystallites, while at raised temperatures progressively smaller nickel oxide crystallites undergo reduction.

The experimental findings described above may constitute a basis for an attempt to explain some possible causes of the poor reducibility of small nickel oxide crystallites, additionally deepened by the presence of water vapor.

First of all, let us recall [6] that nickel oxide reduction requires hydrogen chemisorption on the surface of nickel oxide and the formation of a water molecule from a surface oxygen ion and water desorption. It is only in consequence of these processes that there may occur a reconstruction of the crystalline lattice and a formation of the metal phase (nuclei). Obviously, apart from these stages, it is also necessary that there occurs hydrogen diffusion to the surface of nickel oxide and of the produced water vapor to the gas phase — its significance is especially important when we deal with porous solids. The slowest of the above stages determines the observed reaction rate — when the rate of one of them is nil, the reaction will not take place.

Let us now consider the hypothesis presented in the introduction and quoted from [2].

THE ROLE OF DIFFUSION FACTORS

Most of the nickel oxide crystallites on a support are located in the pores of the carrier, so that the size of these crystallites cannot be larger than the diameters of the pores. As a result, in small pores of the carrier there are small NiO crystallites whereas large NiO crystallites can be found only in large pores and on the outside surface of the carrier. At the same time, NiO crystallites may be found at different distances from the outside surface of the carrier which results from various depths (lengths) of the pores.

The concentration values of hydrogen and water vapor over the surface of NiO crystallites found in the carrier pores are different than in the bulk gaseous phase which is caused by the slower rate of gas diffusion in the pores. The values of the diffusion coefficients of hydrogen and water vapor (Table 1) suggest that the diffusion rate rapidly decreases with the passage from larger to smaller pores. Moreover, the values of the diffusion coefficients of water vapor, which are lower than those of hydrogen, prove that the course of NiO reduction in the pores of the carrier is limited by the rate of the diffusion of the formed water vapor from the pores to the bulk gaseous phase. The diffusion rate is also conditioned by the differences in gas concentration values in the bulk gaseous phase and over the surface of nickel oxide crystallites.

Table 1. Knudsen diffusion coefficients [7]

Temperature [K]	Gas	Pore diameter [nm]				
		1.0	2.0	5.0	10.0	20.0
		Diffusion coefficients [cm^2/s]				
573	H ₂	$8.210 \cdot 10^{-3}$	$1.642 \cdot 10^{-2}$	$4.105 \cdot 10^{-2}$	$8.210 \cdot 10^{-2}$	$1.642 \cdot 10^{-1}$
	H ₂ O	$2.738 \cdot 10^{-3}$	$5.475 \cdot 10^{-3}$	$1.369 \cdot 10^{-2}$	$2.738 \cdot 10^{-2}$	$5.475 \cdot 10^{-2}$
773	H ₂	$9.535 \cdot 10^{-3}$	$1.907 \cdot 10^{-2}$	$4.767 \cdot 10^{-2}$	$9.535 \cdot 10^{-2}$	$1.907 \cdot 10^{-1}$
	H ₂ O	$3.178 \cdot 10^{-3}$	$6.356 \cdot 10^{-3}$	$1.589 \cdot 10^{-2}$	$3.178 \cdot 10^{-2}$	$6.356 \cdot 10^{-2}$

All these factors make the ratio of concentration (partial pressures) of hydrogen and water vapor over large crystallites higher than that over the surface of small crystallites. The difference considerably increases when the depth values of the pores and thus also the length of the diffusion distance are large. Changes in the partial pressures of water vapor and hydrogen over the surface of NiO crystallites in relation to the bulk gaseous phase occur to a much smaller extent in dry hydrogen reduction since water vapor there comes only as a reaction product. However, when additional water vapor is introduced with hydrogen, due to the smaller difference in the concentration values of water in the bulk gaseous phase and over the NiO surface, changes in the partial pressures of water vapor and hydrogen over the NiO surface are the larger, the more water appears in the bulk gaseous phase.

It must have some determined consequences for the course of supported nickel oxide reduction. With a high concentration of water vapor over the surface of NiO crystallites the formation of metal nuclei of dimensions larger than the thermodynamically determined critical size of a nucleus is made much more difficult. It may simply be an action of the reversibility of the reaction of nickel oxide reduction with hydrogen. For this reason, small NiO crystallites, located in narrow and deep pores of a carrier, will remain unreduced. Since water diffusion from the pores becomes even more difficult when it is in the bulk gaseous phase, the reduction will not take place in larger crystallites and those shallower pores.

It seems, however, that the causes of the poor reducibility of small NiO crystallites on $\gamma\text{Al}_2\text{O}_3$ cannot be explained only by the diffusion phenomena discussed above. Small differences in the diffusion coefficients for different

temperatures certainly cannot account for the considerable variety of the sizes of unreduced crystallites at low and high temperatures. Nevertheless, diffusion phenomena may complicate the interpretation of results since they cause changes in gas concentration values over the surfaces of NiO crystallites of various sizes in comparison with the bulk gaseous phase.

NICKEL OXIDE REACTION WITH THE CARRIER

The formation of hardly reducible compounds of nickel oxide with the carrier is that reason for the poor reducibility of supported nickel oxide which is most often quoted in the literature. In the cases when aluminium oxide is employed as a carrier, they usually include compounds of the spinel type NiAl_2O_4 (sometimes non-stoichiometric) or solid solutions of nickel oxide with aluminium oxide or spinel [8, 9]. It is known [10] that the reaction between two solids is the slower, the larger are the reacting particles and that small particles usually react sooner than larger ones. Consequently, if the reaction involves particles of nickel oxide (hydroxide) of different sizes, then within a given time period of calcination small nickel oxide crystallites will form combinations richer in aluminium oxide than large crystallites. In sufficiently large nickel oxide crystallites their substantial portion, which has no direct contact with aluminium oxide, will remain as pure nickel oxide.

Spinel compounds and solid solutions are much less reducible than pure nickel oxide. It results from a much greater energy of binding oxygen ion with cations in NiAl_2O_4 namely, 1012 kJ/mole [11], than in NiO, which is 345 kJ/mole [12]. At the same time, the equilibrium constant of spinel reduction and of solid solutions of nickel and unreducible carrier oxide is smaller than in the case of pure NiO reduction — actually, the smaller it is, the less nickel oxide is there in the solid solution [13].

Since the amount of Al_2O_3 in small nickel oxide crystallites is larger than in crystallites of larger dimensions, they will also be harder to reduce — at higher temperatures and lower partial pressures of water vapor.

STABILIZATION OF NICKEL OXIDE CRYSTALLITES BY THE CARRIER

Considering the effect of the carrier of nickel oxide, one should not neglect the electronic interaction between nickel oxide crystallites and the carrier. When on the surface of the carrier there are single nickel oxide crystallites or their clusters, which do not cover the carrier with a complete layer, it is possible to construct a model based on the principles of the theory on the two solids contact [14]. If two solids, differing in respect to the position of the Fermi level, are in

a very close contact, then some part of electrons may pass from the solid of a higher Fermi level to that of a lower Fermi level. The surfaces of both solids near the site of contact will have different electric potentials. There will appear an electric field reaching the distance of 100–1000 nm in each of the solids considered — it will be strongest in the vicinity of the contact site of the two solids, decreasing with the growing distance away this site.

Such a situation occurs in the NiO— γ -Al₂O₃ system. Due to the presence of structural defects and surface hydroxyl groups, the surface of γ -Al₂O₃ may be regarded as a semiconductor of the n type. Nickel oxide is a semiconductor of the p type. Both oxides have different Fermi levels, which is indicated by the work functions which are smaller for Al₂O₃ than for NiO (Table 2).

Table 2. Work functions [eV] of nickel oxide and aluminium oxide

References	[16]	[17]
NiO	4.20–4.30	5.55
Al ₂ O ₃	3.80–3.90	4.70

Due to this, the surface of nickel oxide crystallite has a negative charge, while some part of the surface of the γ -Al₂O₃ carrier, close to the contact site of both oxides, receives a positive charge (Fig. 3a). In cases of sufficiently large NiO crystallites, the surface in the centre of a crystallite may have no charge at all, just like in the unsupported NiO. When NiO crystallites are smaller than the distance of the electron interaction, the whole surface of NiO has a negative charge. The smaller is the NiO crystallite, the higher is the charge. The zone of positively charged γ -Al₂O₃ surface reaches the same distance from the contact site with NiO crystallites, regardless of their size.

The existence of the electric potential on the surface of semiconductors (i.e., a change in the position of Fermi levels of surfaces) causes changes in gas chemisorption, so that the positive charge (lowering of the position of Fermi level) on the surface increases the chemisorption of the gases which have the donor character, while the negative charge (raising the position of Fermi level) decreases the chemisorption of such gases. Since both gases which occur in NiO reduction, that is, water vapor and hydrogen, are electron donors [18], their amounts chemisorbed on a unit of surface of small NiO crystallites on γ -Al₂O₃ and binding forces are smaller than on the surface of large crystallites, as well as the surface of unsupported NiO crystallites of the same size. This makes it more difficult to detach oxygen from the surface of supported NiO, while in the cases

of small NiO crystallites it may even be impossible, so that as a result they may not undergo reduction to metal.

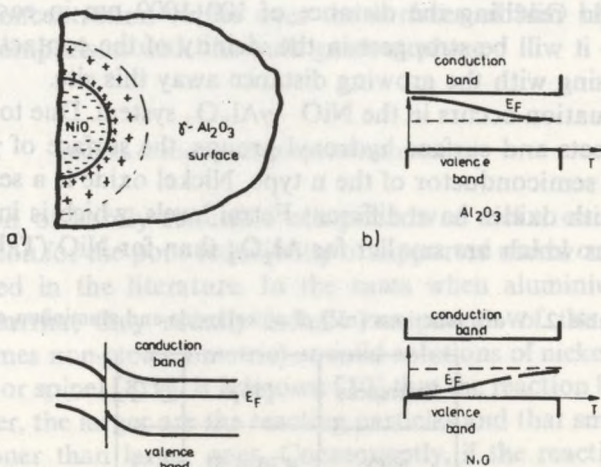


Fig. 3. Electron phenomena in the NiO — γ Al₂O₃ system: a) electron transfer between NiO and γ Al₂O₃; b) temperature effect of the position of Fermi levels in Al₂O₃ and NiO

The rise in Fermi level on NiO surface is also caused by water vapor chemisorption [18], which creates additional difficulty in detaching oxygen from the NiO crystallite lattice and thus in forming metal nuclei in subsequent stages. It is a likely reason for the lengthening of the induction period and slowing down the rate of unsupported NiO reduction when wet hydrogen is employed for this purpose.

The chemisorption of water vapor present during the reduction brings about an increase in the number of surface hydroxyl groups on γ Al₂O₃. Due to the positive charge of the Al₂O₃ surface near nickel oxide crystallites, there occurs a considerable increase in water chemisorption at this site when compared with the remaining surface of the carrier. NiO crystallites are thus placed in a dense surrounding of surface hydroxyl groups. By raising Fermi level, water chemisorption on γ Al₂O₃ at the same time causes an increase in the electric potential difference on the surfaces of the carrier and NiO crystallites. Practically, it means that the negative charge of NiO surface is increased, causing the increase of the size of the crystallites, oxygen detachment from which becomes impossible and their reduction does not take place. The increase in the partial pressure of water vapor produces a nonlinear (just as its chemisorption isotherm is nonlinear) increase in the amount of chemisorbed water vapor as well

as in the number of hydroxyl groups on $\gamma\text{Al}_2\text{O}_3$, so that in consequence the sizes of unreducible nickel oxide crystallites also grow.

The position of Fermi level in semiconductors is dependent on temperature and at a raised temperature it is moved towards the centre of the energy gap between the valence band and conductivity band (Fig. 3b) [19]. In semiconductors of the n type (Al_2O_3) this means a lowering of Fermi level, while in semiconductors of the p type (NiO) — a rise in Fermi level. When the NiO — $\gamma\text{Al}_2\text{O}_3$ system is in a raised temperature, then the difference in the Fermi levels of NiO and $\gamma\text{Al}_2\text{O}_3$ is smaller than in a lower temperature. It means that at higher temperatures the electric potentials of the surface of NiO crystallites and the surrounding surface of Al_2O_3 are smaller, which, in consequence, enables the reduction of supported nickel oxide crystallites smaller than at low temperatures.

CONCLUSIONS

So far the literature data and results reported in our paper indicate that the smaller reactivity of supported NiO , when compared with unsupported NiO , is connected with its very great dispersion. The causes of the poor reducibility of small crystallites of supported NiO should be looked for mainly in their effective reaction with the carrier and in the strong electron interaction between NiO and the carrier. In the light of the above considerations, small NiO crystallites have more chances to react with the carrier and form hardly reducible compounds than large crystallites. At the same time, the electron interaction is more clearly visible in cases of small crystallites of supported nickel oxide. We are of the opinion that the role of water vapor in supported NiO reduction may consist in enabling the reversibility of the reaction of reduction of nickel oxide crystallites of various sizes (in different degrees of reaction with the carrier) which are characterized by different equilibrium constants and in heightening the electron interaction of NiO crystallites with the support.

Both interpretations of experimental results proposed above also provide a basis for an explanation of the easier reduction of the NiO — SiO_2 system than of the NiO — $\gamma\text{Al}_2\text{O}_3$ system or of the still more difficult reduction of the NiO — MgO system. Magnesium oxide forms bindings with NiO more easily than $\gamma\text{Al}_2\text{O}_3$, while the latter, in turn, more easily than SiO_2 . The higher value of the work function of SiO_2 , 5.0 eV [17] than of Al_2O_3 , and hence also the smaller difference between the work functions of SiO_2 and NiO than between Al_2O_3 and NiO , also contribute to a weaker stabilization of NiO crystallites by the SiO_2 carrier. The opposite situation occurs in the case of MgO , whose work function is about 3.3 eV [15] so that the stabilization of nickel oxide crystallites is stronger than on the $\gamma\text{Al}_2\text{O}_3$ carrier.

The confirmation of the validity of the proposed interpretations of experimental results still requires additional, difficult investigations which are further complicated by carrier porosity and related diffusion phenomena.

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STRESZCZENIE

Mniejsza reaktywność nośnikowego NiO w porównaniu z beznosnikowym NiO związana jest z jego bardzo dużą dyspersją. Przyczyn trudnej redukcji małych krystalitów nośnikowego NiO szukać trzeba przede wszystkim w ich głębokiej reakcji z nośnikiem oraz silnych oddziaływaniach elektronowych pomiędzy NiO i nośnikiem. Rola pary wodnej w redukcji nośnikowego NiO polegać może na umożliwieniu odwracalności reakcji redukcji krystalitów NiO o różnej wielkości, które charakteryzują się różnymi stałymi równowagi oraz na zwiększeniu oddziaływań elektronowych krystalitów NiO z z nośnikiem.