THE EFFECT OF SUPERSTOICHIOMETRIC OXYGEN ON THE CATALYTIC, ADSORPTION, AND ELECTRICAL PROPERTIES OF NICKEL OXIDE

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THE EFFECT OF SUPERSTOICHIOMETRIC OXYGEN ON THE CATALYTIC, ADSORPTION, AND ELECTRICAL PROPERTIES OF NICKEL OXIDE

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This work arose as a result of investigations of the catalytic, adsorption, and electrical properties of nickel oxide samples with different electrical conductivity ([1]). Nickel samples obtained by calcination in air at different temperatures contain different amounts of oxygen in excess of stoichiometry, the fraction of which decreases with increasing decomposition temperature of the initial salt. Simultaneously with an increase in the percentage content of excess oxygen, the color of nickel oxide changes from green to black, as do some other properties, for example, electrical conductivity, magnetic susceptibility, catalytic activity, etc. ([1]).

1. Samples of nickel oxide were obtained by calcining nickel carbonate, previously pelletized at a pressure of 4000 atm, at temperatures of 500, 600, 700, 800, and 900° for 3 hours, with continuous blowing of purified air. The color of the samples changed from black NiO (500°) to light-green NiO (900°). The values of the specific surfaces were determined by the BET method from equilibrium isotherms of physical adsorption of krypton at the temperature of liquid nitrogen (−195°).

Table 1

Specific surfaces of NiO of different calcination and the initial composition of the samples

Catalyst	S_1, m^2/g (by krypton)	Initial composition
NiO (900°)	2.0	$Ni_1O_{0.997}$
NiO (800°)	3.5	–
NiO (700°)	13.0	$Ni_1O_{1.07}$
NiO (600°)	17.5	–
NiO (500°)	30.5	$Ni_1O_{1.13}$

Oxygen in excess of stoichiometry was determined by reduction of NiO in a

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

stream of hydrogen at a temperature of 400°. These data are summarized in Table 1. The electrical conductivity was determined by the method described earlier (^{2}).

Table 2

Catalyst	E, kcal/mol	R, ohm • cm
NiO (900°)	30	$7.0 \cdot 10^5$
NiO (800°)	25	$6.8 \cdot 10^4$
NiO (700°)	21	$4.0 \cdot 10^4$
NiO (600°)	–	$8.9 \cdot 10^3$
NiO (500°)	15	$6.9 \cdot 10^3$

Table 2 gives data on the specific electrical conductivity at 25° and on the activation energy of electrical conductivity, measured in vacuum in the temperature range from room temperature to 300° for NiO samples of different calcination. It can be seen that the electrical conductivity of the extreme samples differs by two orders of magnitude, while the activation energy changes by 15 kcal/mol.

2. The catalytic reaction of CO oxidation on a stoichiometric mixture ($2CO + O_2$) was studied in a vacuum apparatus under static conditions at a pressure of 0.5 mm Hg. The reaction product CO_2 was frozen out in a U-shaped trap cooled with liquid nitrogen. The oxidation kinetics for all

samples corresponded to a first-order equation. Figure 1 presents the temperature dependence of the rate constant for CO oxidation on the samples studied. Table 3 gives the values of the activation energy of CO oxidation, the pre-exponential constants, and the specific rate constants K_1 at 24°.

Fig. 1. Dependence of the logarithm of the rate constant for CO oxidation on reciprocal temperature for NiO of different calcination: 1 –500°, 2 –600°, 3 – 800°, 4 –900°

Fig. 2. Kinetic curves of CO adsorption at $t = 24°$ for NiO of different calcination: 1 –500°, 2 –800°

It follows from Table 3 that on all NiO catalysts calcined in the temperature range from 500 to 800°, the reaction proceeds with practically identical activation energies, but with different initial rates of the process. The rate constant m at 24° on the NiO (800°) catalyst is approximately three times greater than

Fig. 3

Figure 3: Fig. 3

on NiO (500°). The increase in the rate constant in this case is associated with an increase in the pre-exponential constant K_0. On the NiO (900°) sample, which in composition is close to stoichiometric, the activation energy of the CO oxidation reaction increases by almost 3 kcal/mole.

Table 3

Catalyst	K_0	K_1 at 24°	E, kcal/mole
NiO (900°)	$2 \cdot 10^3$	0.11	5.7
NiO (800°)	$6.4 \cdot 10$	0.37	3.0
NiO (600°)	$3.4 \cdot 10$	0.20	3.0
NiO (500°)	$2.2 \cdot 10$	0.11	3.0

The adsorption of oxygen, CO, and acetylene was measured on NiO (800°) and NiO (500°). In terms of the character of electron transfer, O_2 is an electron acceptor, while CO and C_2H_2 are electron-donor gases. CO adsorption was studied at room temperature and is shown in Fig. 2, from which it is evident that the adsorption rate of these gases and the total adsorbed amount decrease slightly for the NiO (500°) sample as compared with NiO (800°). The adsorption of C_2H_2 proceeded analogously. Oxygen adsorption, measured at 300°, is practically identical for NiO (800°) and NiO (500°), as shown in Fig. 3.

Fig. 3. Kinetic curves of oxygen adsorption at $t = 300°$ for NiO of different calcination: 1 –500°, 2 –800°

3. When different calcination temperatures were applied to the initial nickel carbonate, catalysts were obtained that differed in their composition from stoichiometry. As we have shown, the deviation from stoichiometry is connected with an excess of oxygen. The excess oxygen may be located at lattice sites in the form of negative divalent anions. For each such anion in the nickel oxide lattice there is formed one cation vacancy and, to preserve the neutrality of the lattice, two Ni^{3+} ions near the vacant site.

With an increase in the amount of excess oxygen, and consequently of Ni^{3+} ions, the rate of the CO oxidation process decreases, just as it does on solid solutions of NiO with an addition of lithium oxide (3). However, if the decrease in the rate of the process on NiO($\mathrm{Li_2O}$) samples is associated with a change in the activation energy of the process, in the present case it is caused by a decrease in the pre-exponential constant K_0 of the reaction-rate constant. The change in K_0 proceeds as if in parallel with the change in adsorption of the main reaction component, CO. It may be assumed that the limiting stage of the reaction is CO adsorption. The absence of a relationship (within the range 800–500°) between the activation energy of the catalytic process E_{cat} and the activation energy of electrical conductivity E_σ points to a different mechanism of interrelation between these two phenomena in the given system.

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REFERENCES

[1] N. P. Keier, S. Z. Roginskii, I. S. Sazonova, *DAN*, **106**, 859 (1956); N. P. Keier, L. N. Kutseva, *DAN*, **117**, No. 2, 259 (1957).
[2] W. Klemm, K. Hass, *Zs. anorg. Chem.*, **219**, 82 (1934); M. Le Blanc, H. Sachse, *Zs. anorg. Chem.*, **168**, 15 (1927); *Phys. Zs.*, **32**, 887 (1931); M. Prasad, M. G. Tendulkar, *J. Chem. Soc.*, 1931, 1403, 1407.
[3] N. P. Keier, L. N. Kutseva, *Izv. AN SSSR, OKhN*, 1959, No. 5, 797.
[4] I. S. Sazonova, Dissertation, IFKh AN SSSR, 1957.

Note: Figure translations are in progress. See original paper for figures.