Physical Chemistry

1964

SovietRxiv

Abstract

Full Text

Physical Chemistry

M. D. Shibanova, G. M. Zhabrova

Application of the Emanation Method to the Investigation of the Structure of Zinc Oxide and Nickelous Oxide with Additions of Lithium and Gallium Oxides

(Presented by Academician V. N. Kondrat' ev, December 6, 1963)

The development of electronic concepts in adsorption and catalysis has led to the undertaking of numerous experimental studies on the influence of additives on the catalytic and electronic properties of semiconductor catalysts, in particular oxides.

Of particular interest was the investigation and comparison of these properties for two oxide semiconductor catalysts: an electronic and a hole conductor (zinc oxide and nickelous oxide), in which additions of metal oxides of greater or lesser valence than the valences of ZnO and NiO led to the formation of solid solutions with the initial oxides and could create positively or negatively charged defects ([1–7]).

When cations of a different valence, such as, for example, Li^+, dissolve in nickelous oxide, substitutional solid solutions are formed and the concentration of trivalent nickel in the bulk and on the surface of the semiconductor changes ([8]).

For zinc oxide, upon dissolution of cations of lower or higher valence than Zn^{2+}, one may expect a significant increase or decrease in the defectiveness of the crystal-lattice structure caused by "enrichment" or "depletion" of its interstitial Zn^+. Similar phenomena were noted by Schwab ([9]) in studying the kinetics of substitution of zinc ions in ZnO by copper ions (from copper sulfate) in the solid phase. The addition of lithium ions to zinc oxide caused an increase in the rate of the exchange reaction. The introduction of gallium ions into ZnO had an inhibiting effect.

In the present investigation an attempt was made to apply the emanation method, which is very sensitive to various kinds of defects and disturbances of the crystal lattice of solids, to the study of changes in the structure of zinc oxide and nickelous oxide caused by the introduction of additions of lithium and gallium oxides. The method is based on introducing into the solid under study radioactive isotopes of radium or thorium, which in their successive radioactive decay generate inert radioactive gases—emanations: radon and thoron. The em-

Fig. 1. Change in emanating ability with temperature for the original zinc oxide (1) and for zinc oxide modified with lithium oxide (2) and gallium oxide (3)

Figure 1: Fig. 1. Change in emanating ability with temperature for the original zinc oxide (1) and for zinc oxide modified with lithium oxide (2) and gallium oxide (3)

anating ability, i.e., the degree of release of emanation from the solid, depends very strongly on the state of its crystal lattice.

Luminescent zinc oxide and nickelous oxide obtained by decomposition of nickel hydroxide at a temperature of 400° for 2 hours were used as the objects of investigation. The modifying additives were introduced by impregnating pastes of zinc and nickel hydroxides, previously labeled with radiothorium, with solutions of gallium nitrate salts or lithium oxalate, in amounts of one to two atomic percent. The preparations prepared in this way were thoroughly dried and then calcined at a temperature of 450° for 8–10 hours. The samples of the modified oxides were then placed in a quartz apparatus inserted into an electric furnace equipped with a regulator for uniform temperature rise. During the continuous rise in temperature (10° per minute), a stream of nitrogen was passed through the apparatus; its rate was selected in such a way that, during measurement of the emanation released, the maximum fraction of activity was recorded. Measurements of thorium emanation were carried out in an apparatus with automatic recording of α-activity.

With the introduction of 2 at.% thorium, X-ray structural analysis did not show

changes in the lattice parameters of the oxides studied. Without touching on the question of possible structural changes in oxides with an addition of thorium, we shall note that, since the indicator element (thorium) was present in all the samples studied, the observed effects could not have been caused by the presence of this additive.

Figure 1 shows the change in the emanating ability of the original zinc oxide and of zinc oxide with additions of lithium and gallium oxides. As follows from the figure, a considerable increase in emanation, apparently due to loosening of the crystal lattice, begins for the original ZnO sample (curve 1) close to the Tammann temperature (850-900°). With the introduction of lithium oxide, the increase with temperature in the amount of emanation released from zinc oxide is more sharply pronounced, and the temperature at which mobility of the crystal-lattice ions begins to appear is lowered (curve 2). The addition of an oxide of a metal of higher valence, in particular gallium oxide, considerably slows the increase in the emanating ability of zinc oxide with rising temperature (curve 3). The effects obtained are reversible, since repeated calcination of zinc oxide samples with introduced additions, with some decrease in the absolute magnitude of emanation, gives similar results.

Fig. 2. Dependence of the emanating ability of ZnO at T = 930° on the amount of lithium oxide introduced

Figure 2: Fig. 2. Dependence of the emanating ability of ZnO at T = 930° on the amount of lithium oxide introduced

Fig. 1. Change in emanating ability with temperature for the original zinc oxide (1) and for zinc oxide modified with lithium oxide (2) and gallium oxide (3)

These data indicate the appearance of considerable defectiveness in the zinc-oxide lattice upon introduction of Li^+ and its decrease upon introduction of Ga^{3+}. The repeated reproduction of the effects obtained on one and the same sample is evidently connected with the formation of stable structures of the solid-solution type, since otherwise each subsequent calcination would lead to ever greater removal of volatile lithium compounds and to a change in the observed effects.

Fig. 2. Dependence of the emanating ability of ZnO at $T = 930°$ on the amount of lithium oxide introduced

Thus, the data obtained by the emanation method qualitatively confirm the notions of an increase in the number of interstitial Zn^+ ions formed upon introduction of an Li_2O addition into zinc oxide, leading to an increase in the defectiveness of the crystal lattice of zinc oxide, and of a decrease in the number of Zn^+ ions and, correspondingly, in the defectiveness of the crystal lattice of this oxide upon introduction of an Ga_2O_3 addition.

It was of interest, by means of the emanation method, to estimate the maximum value of the solubility of lithium oxide in zinc oxide. For this purpose the concentration of the introduced additive was varied from 0.01 to 5 at.% lithium (see Fig. 2). Increasing the lithium content above 1 at.% does not lead to a further growth of emanation. Spectral analysis showed that, upon introduction of this amount of lithium oxide, the content of lithium ions in zinc oxide is $\sim$ 0.3–0.5 at.% (the remaining part, evidently,

is removed during calcination of the sample). Apparently, the solubility of lithium oxide in powdered zinc oxide samples can be estimated at no more than 0.5 at.% (calculated as Li).

Let us recall that, according to the data of Lander (^{10}), who studied the electrical conductivity of a zinc oxide single crystal with lithium added in zinc vapor, the highest concentrations of dissolved lithium in ZnO at $T = 600°$ were $1 \cdot 10^{18}$–$1 \cdot 10^{19}$ atoms per 1 cm^3, which corresponds approximately to 0.01–0.1 at.% Li. X-ray structural study of the samples we investigated did not reveal any change in the parameters of the zinc oxide crystal lattice even upon the introduction of 8% Li, which indicates the absence of substitutional solid solutions. Evidently, the emanating ability proved to be very sensitive to the formation of surface

Figure 3

Figure 3: Figure 3

Figure 4

Figure 4: Figure 4

interstitial solutions. The penetration depth in ZnO of the indicating element (ThX, formed during the decay of RdTh) is, according to our calculations, 300 Å. Evidently, dissolved lithium penetrates to the same depth. The assumption of the formation of a solid interstitial solution of Li_2O in the near-surface layer of ZnO is consistent with data on the electrical conductivity and electron work function for zinc oxide samples with Li_2O additions ([11]), which are explained by a difference in the Li_2O content in the layer of the solid interstitial solution.

Fig. 3. Change in the emanating ability of the initial nickel oxide sample (1) and of nickel oxide with an addition of lithium (2), gallium (3), and upon repeated heating of NiO with a gallium addition (4)

The change in emanation with increasing temperature for nickel oxide samples with additions of lithium and gallium oxides is shown in Fig. 3. The emanating ability of pure NiO (curve 1) increases slightly at a temperature of about 1000°. The addition of lithium oxide (Fig. 3, 2) hardly changes the course of the curve, while Ga_2O_3 causes a sharp rise in emanating ability in the range 500–700° (curve 3). Upon repeated calcination of the sample in this temperature interval, no increase in emanation is observed, i.e., the effect is irreversible (curve 4).

It was established that the magnitude of the effect is related to the amount of Ga_2O_3 additive introduced into nickel oxide. As follows from Fig. 4, the height of the peak on the emanogram increases with increasing Ga content, while the temperature range corresponding to the maximum of emanation does not change with the amount of additive.

Fig. 4. Change in the emanating ability with temperature of nickel oxide samples with a gallium addition: 0.1 at.% (1), 0.5 at.% (2), 1 at.% (3)

Taking into account the simultaneous change in color from black to gray-green, it could be assumed that the appearance of a maximum of emanating ability during calcination of nickel oxide samples with gallium oxide additions at a temperature of 500–700° is associated with the process of restructuring of the nickel oxide structure, accompanied by the release of excess oxygen ([12]).

Let us note that, according to thermogravimetric-analysis data, the removal of excess oxygen from NiO samples prepared in different ways occurs at $T = 400$ –600° ([13]). The superstoichiometric, excess oxygen, the amount of which is proportional to the amount of Ni^{3+} ions, was determined by the iodometric method both upon partial and upon complete dissolution of the samples in hydrochloric acid ([14]). In the first case, the excess of oxygen contained in the near-surface layer of the sample was determined. It was established that for nickel oxide with an addition of 1 at.% gallium and 2 at.% thorium, calcined at 400°, the greater part (1.4 at.%) of the nonstoichiometric oxygen is located on the surface. For a nickel oxide sample calcined at 400°, with additions of 1 at.% lithium and 2 at.% thorium, only about 0.7 at.% of excess oxygen is located on the surface (2.5–3 at.%), contained both on the surface and in the bulk of nickel oxide samples with additions of gallium and thorium oxides and lithium and thorium oxides. Calcination to 1100° decreased the amount of excess oxygen on the surface of these samples to 0.2 at.%. We shall mention that in the paper by A. Bielanski, Deren, and others ([15]) it is noted that nickel oxide samples with additions of ions of monovalent and trivalent metals differ in the content and in the form of occurrence of excess, superstoichiometric oxygen. They established that nickel oxide with an addition of iron oxide, calcined above 800°, contains practically no excess oxygen, and that upon calcination at 600° the greatest amount of it is found per unit surface, decreasing rapidly with an increase in the calcination temperature. A nickel oxide sample with an addition of lithium oxide holds the excess oxygen more firmly and is capable of desorbing part of this oxygen only at a calcination temperature above 900°.

The maximum of the emanating capacity in the region of 500–700°, shown in Figs. 3 and 4, is apparently associated with the formation of a substitutional solid solution of nickel oxide with the introduced addition of gallium oxide, with the accompanying homogenization of the addition and liberation of excess oxygen. Naturally, repeated calcination no longer changes the structure of the sample and therefore has no effect on its emanating capacity.

In conclusion, we shall mention that the introduction, by coprecipitation, of 2% magnesium oxide into zinc oxide and nickel oxide did not have a noticeable effect on their emanating capacity.

Thus, the application of the emanation method to the study of zinc oxide and nickel oxide with additions of cations of different valence (Li^{+}, Ga^{3+}) made it possible to obtain new information on the character of the structure of these oxides, the temperature region of formation of solid solutions, and the order of magnitude of the solubility of the introduced additions.

Part of the experimental work was carried out by Yu. I. Chernyshenko, for which the authors express their gratitude to him.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
21 XI 1963

CITED LITERATURE

1. J. H. de Boer, I. W. Verwey, Proc. Phys. Soc., **49**, 5971 (1937); I. W. Verwey, P. W. Haayman, F. C. Romeijn, Chem. Weekblad., **44**, 705

(1948).

2. C. Wagner, J. Chem. Phys., **18**, 69 (1950).

3. G. Parravano, J. Am. Chem. Soc., **75**, 1448, 1452 (1953).

4. G. M. Schwab, J. Block, Zs. phys. Chem., N. F., No. 1, 42 (1954); Zs. Elektrochem., No. 9, 756 (1954).

5. N. P. Keier, S. Z. Roginskii, I. S. Sazanova, DAN, **106**, 859 (1956); Izv. AN SSSR, ser. fiz., **21**, 183 (1957).

6. A. Cimino, M. Marezio, A. Santaro, Naturwiss., **44**, H–12, 348 (1957).

7. V. I. Gorodetskii, L. A. Kasatkina, V. Yu. Levin, Kinetika i kataliz, **3**, 422 (1963).

8. S. Z. Roginskii, Khim. nauka i prom. **2**, 154 (1957).

9. G. M. Schwab, Zs. phys. Chem., N. F., No. 9, 127 (1956).

10. I. I. Lander, J. Phys. Chem. Solids, **15**, 324 (1960).

11. V. I. Vladimirova, E. Kh. Enikeev et al., DAN, **131**, 342 (1960).

12. J. Jermen, *Heterogeneous Catalysis*, IL, 1961, p. 125.

13. G. Maxim, T. Braun, J. Phys. Chem. Solids, **24**, 537 (1963).

14. H. Gossel, Zs. Elektrochem., B–65, No. 1 (1961).

15. A. Bielanski, I. Derén et al., Trans. Farad. Soc., **85**, 166 (1962).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.