

REDUCTION OF MIXED COPPER AND ZINC OXIDES

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The reduction of mixed copper and zinc oxides with hydrogen was studied thermogravimetrically in the temperature range of 290–500°C. Different oxide mixtures were prepared by thermal decomposition of mixed crystalline nitrates of the both components on air at 350°C. Only copper oxide is reduced in the mentioned temperature range. Its reduction rate is a function of the composition and decreases monotonously with increasing content of zinc oxide. The kinetics of the reduction can be described quantitatively in the whole composition range by a modified Prout–Tompkins equation. The mutual interaction of the components, which do not form a solid solution, is conditioned by contact phenomena on the phase boundary and the semiconducting character of the both oxides. The zinc oxide modifies the equilibrium states of oxygen present in the system and the stoichiometry of the copper oxide. A correlation between the found dependences and the two-component systems studied earlier was found on the basis of the electron theory of adsorption on semiconductors.

Besides the study of the kinetics and mechanism of reduction of pure oxides, an increasing attention has been paid to the reduction of two-component oxide systems, where the reduction of only one component takes place^{1,2}. The results of certain studies^{3,4} suggest that the nonreducible admixture can substantially influence the kinetics of reduction of the other component even in such a composition range where the both oxides do not form solid solutions. The character of the mutual influence of the both components is, however, a complicated function of many factors and is usually specific for every given system.

The object of the present work was a systematic study of the reduction of mixed copper and zinc oxides and the comparison of the kinetics of their reduction with that of other two-component systems with analogous semiconducting properties.

EXPERIMENTAL

Mixed oxides of different composition were prepared by thermal decomposition of mixed nitrates. Saturated solutions of nitrates of both metals (of reagent grade) were mixed in the desired ratios, evaporated on a sand bath, and the crystalline residue was heated open to the air for 4 h in an electric resistance furnace at 350°C. To follow the influence of the decomposition temperature on the reduction kinetics, also several samples of varying composition were prepared so that a portion of the mixed nitrates was thermally decomposed at 280 or 700°C under analogous conditions. After grinding in an agate mortar, a fraction with the particle diameters in the range 0.05–0.2 mm was separated on sieves for further experiments.

The content of the both metals in the samples was determined complexometrically (Table 1). The specific surface areas were measured by nitrogen adsorption at low temperatures. The crystallographic structure of the samples was studied by the Debye-Scherrer method or by the method of the reverse beam. The content of the non-stoichiometric oxygen was determined iodometrically⁵. The reduction was studied in the temperature range 290–500°C, its kinetics thermogravimetrically on the described apparatus⁶. Conditions were found where the rate and time course of the reduction are independent of the rate of flow of hydrogen at an arbitrary composition of the sample, which weighed 50 mg. In this region is the rate of flow of 56 ml/min used in our experiments.

RESULTS

It follows from the analysis (Table I) that even the temperature of 280°C is sufficient for the decomposition of the mixed nitrates and the preparation of the oxides. At temperatures higher than 500°C, the copper oxide decomposes in the presence of the other component under formation of copper. This was proved by microstructural analysis of samples obtained by decomposition of mixed nitrates at higher temperatures than the samples of the basic series. With the oxides of the basic series (prepared at 350°C), only selective reflexions were recorded corresponding to the copper oxide

TABLE I

Composition and Specific Surface of Mixed Copper and Zinc Oxides

Sample	Weight. %				Mol. %		S m ² /g
	Cu	Zn	CuO	ZnO	CuO	ZnO	
1	79.55	—	99.54	—	100.0	—	0.32
2	79.13	0.78	98.91	0.96	99.0	1.0	0.26
3	70.94	8.69	88.67	10.77	89.4	10.6	0.34
4	63.21	16.63	79.01	20.62	79.7	20.3	0.32
5	55.40	24.52	69.25	30.40	69.9	30.1	0.36
6	47.12	32.82	58.90	40.69	59.7	40.3	0.22
7	40.79	39.21	50.98	48.62	51.7	48.3	0.13
8	31.11	48.06	38.88	59.59	40.0	60.0	0.17
9	22.72	53.78	28.40	66.70	30.3	69.7	0.17
10	15.25	64.85	19.06	80.39	19.5	80.5	0.15
11	6.39	73.77	7.98	91.47	8.2	91.8	0.10
12	0.76	79.48	0.95	98.56	1.0	99.0	0.08
13	—	80.15	—	99.78	—	100.0	0.02
^a 7 ₂₈₀	38.39	41.62	47.98	51.61	48.5	51.5	—

^a The sample was prepared by nitrates decomposition at 280°C.

and zinc oxide. It was found by the reverse beam method that the parameters of the hexagonal lattice of zinc oxide are not influenced by the increasing content of copper oxide. The deviations of the found values from the theoretical are within $\pm 0.05\%$.

The studied system is characterized by low values of the specific surface areas and their little dependence on the composition of the mixed oxides (Table I). Examination of the samples with a scanning electron microscope revealed a high degree of aggregation of elementary pyramidal crystallites, practically without cracks and pores, typical for oxides of nitrate origin with small specific surfaces⁷.

The presence of ionogenic superstoichiometrical oxygen was proved only with the first two samples of the series (Table I): 0.045 (sample 1) and 0.009 wt.% oxygen (sample 2). With other samples, the content of superstoichiometric oxygen is zero.

In the temperature range under study the samples were reduced at a measurable rate up to a content of 8.20 mol % CuO (sample 11, Table I). The maximum degree of reduction at a given composition is independent of the temperature in the range 350–500°C. In Fig. 1 is shown the dependence of the reduced fraction at 500°C on the composition, where 100% corresponds to the theoretical value calculated from the sample weight and composition under the assumption that the copper oxide present in the mixture is completely reduced. The copper oxide is under the given conditions practically quantitatively reduced including sample 7 (51.7 mol % CuO) and is the only reducible component of the mixture. Its rate of reduction is strongly

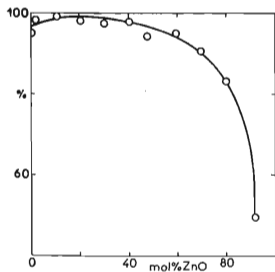


FIG. 1
Dependence of Percent Reduction at 500°C
on Composition of Samples

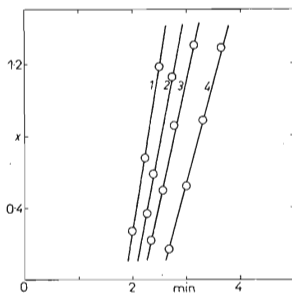


FIG. 2
Application of Modified Prout-Tompkins
Equation to Reduction of Sample 3 at
Different Temperatures

$X = \log [(0.3 + \alpha)/(1 - \alpha)]$; 1 380°C, 2
350°C, 3 320°C, 4 290°C.

influenced by the presence of the other component and is a function of the composition. In a mechanical mixture of the both pure oxides in an arbitrary ratio, the zinc oxide acts as an inert admixture and the course of the reaction corresponds to the reduction of the pure copper oxide.

The kinetics of the reduction of the oxide mixture can be described quantitatively by the Prout-Tompkins equation modified by Bond⁸ in the form $\log [(x + \alpha)/(1 - \alpha)] = kt$, which describes well the reduction of the pure copper oxide. Here α denotes degree of the reduction at time t , k rate constant, and x is between 0.3 and 0.6 depending on α value corresponding to the maximum reaction rate. This equation applies in a wide range of $\alpha = 0.03-0.8$ with $x = 0.3$ (Fig. 2). The apparent activation energy of the reduction was calculated from the temperature dependence of the rate constant as $E_a = 5.20 \cdot 10^4$ J/mol for sample 1 (pure CuO) in accord with the literature^{8,9}. The reduction of the mixed oxides is characterized by an average activation energy of $(6.82 \pm 1.67) \cdot 10^4$ J/mol; somewhat higher values correspond to samples with a higher content of zinc oxide.

The dependence of the rate constant on the composition is shown in Fig. 3; with increasing content of zinc oxide the induction period becomes longer and the reaction rate decreases monotonously. A similar course shows the dependence of the maximum reduction rate on the composition. From this dependence at various temperatures

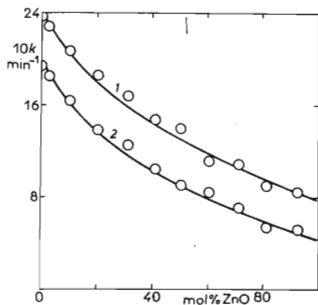


FIG. 3

Dependence of Rate Constant of Reduction on Composition at Different Temperatures
1 380°C, 2 350°C.

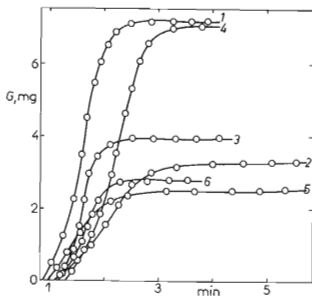


FIG. 4

Time Courses of Primary Reduction, Oxidation and Secondary Reduction of Sample 5 at Different Temperatures

1, 4 Primary reduction; 2, 5 oxidation;
3, 6 secondary reduction; 1-3 380°C,
4-6 320°C.

it follows that in the region where the reaction attains its maximum rate, it passes temporarily from the kinetic to the diffusion-controlled regime. This is supported by the value of the apparent activation energy calculated from the temperature dependence of the maximum reduction rate, which attains a value of $2.01 \cdot 10^4$ J/mol on the average. This effect is a result of a strong local overheating of the sample by the exothermic reaction causing a pronounced increase of the reaction rate.

To study the influence of the partial pressure of hydrogen on the reduction kinetics, some samples were reduced by a mixture of hydrogen and nitrogen at a constant rate of flow of 56 ml/min. In the range of partial pressures up to $p_{\text{H}_2} = 66.6$ kPa the reaction rate increases linearly with p_{H_2} and attains a limiting value at higher pressures.

Selected samples were after the reduction oxidized in a flow of dry air to attain a constant weight, and then reduced again by hydrogen. All three processes took place at a constant temperature of 320 or 380°C (Fig. 4). The degree of oxidation of the sample increases with the temperature but is only little dependent on its composition. During the secondary reduction, which proceeds at a higher rate than the primary one, only that portion of the oxide is reduced which was formed by the oxidation of the metal. In contrast to the both reductions, the oxidation is characterized by a very slow rate during the final stage up to the attainment of a constant weight increment.

A preliminary thermal treatment of the samples in an inert atmosphere for 1 h up to 500°C has no influence on the reduction kinetics. Also the calcination temperature during the preparation of the samples up to 500°C practically does not influence the course of the reduction. At higher treatment temperatures, decomposition of the copper oxide in the presence of the other component takes place.

DISCUSSION

It follows from our results that in the studied two-component system under the given conditions only copper oxide is reduced. In older communications^{10,11} the reduction of mixed oxides of copper and zinc and their mechanical mixtures with hydrogen was reported, where both components were reduced under formation of an alloy, or a compound. The starting mixtures and the experimental conditions were, however, different from those in our work. In a mechanical mixture in an arbitrary ratio, the zinc oxide is an inert admixture which practically does not influence the reduction rate of the copper oxide. This is in support of the earlier conclusions¹² that the retarding influence of the nonreducible component is not due to a mere blocking of the reactive interface on which this component accumulates. The mutual influencing of both components in the mixed oxide, which is manifested by a pronounced dependence of the reaction rate on the composition and by a change of the activation energy of the reduction, is a function of complex contact phenomena on the interface. The results of microstructural analysis and the values of the maximum weight decre-

ments during the reduction, corresponding in the whole range of the composition only to the reduction of copper oxide, lead to the assumption that the both components do not form a homogeneous solid solution. In such a system it is not possible to assign the oxygen uniquely to one of the components and the degree of reduction of the solid solution would be hence higher than the theoretical value of α calculated for the reduction of a single component.

From the point of view of the electrical conductivity, zinc oxide is a typical n-type semiconductor. Stoichiometrical copper oxide is assumed to have a characteristic type of semiconductivity¹³ where the electronic and hole conductivity are in equilibrium. According to the conditions of the preparation, the first or the second type of conductivity can prevail. It follows from experimental results that the samples studied in the present work contain nonstoichiometrical copper oxide of p-type semiconductivity evidenced by the sign of the thermoelectric voltage. In accord with this are the results of the determination of superstoichiometrical oxygen in dependence on the composition; the studied two component system can be considered analogous to the nickel oxide–zinc oxide system studied earlier^{7,12}. With increasing content of zinc oxide in the samples, its free electrons are localized on disorders, *i.e.* Cu^{3+} ions, which are simultaneously reduced, $\text{Cu}^{3+} + e^- \rightarrow \text{Cu}^{2+}$. As a result, the concentrations of both Cu^{3+} and ionogenic superstoichiometric oxygen decrease. It is also possible that the electrons are localized on Cu^{2+} ions with the reaction $\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+$, which results in the formation of some cuprous oxide decreasing the equilibrium tension of cupric oxide¹⁴. If we assume at higher temperatures (during thermal treatment of the samples or calcination of the starting salts) a partial dissociation of cupric oxide under formation of a lower valence oxide, then in the presence of zinc oxide the electrons can be localized on Cu^+ ions with the reaction $\text{Cu}^+ + e^- \rightarrow \text{Cu}$. In this way the zinc oxide probably supports the thermal dissociation of the copper oxide and the formation of copper. The presence of the latter was proved in the case of mixed samples treated at higher temperatures by the X-ray analysis. The fact that zinc oxide modifies the equilibrium state of oxygen in the system primarily by removing oxygen follows also from other experimental results. From the comparison of reoxidation experiments with samples⁴ of the previously studied series $\text{CuO}-\text{Cr}_2\text{O}_3$ (p, p-type semiconductors) follow much longer times for the oxidation of copper (formed by primary reduction) to a constant degree in the case of the copper oxide–zinc oxide system.

As already mentioned, with increasing content of zinc oxide the stoichiometry of copper oxide is modified by reduction of Cu^{3+} ions and a stoichiometrization of the system takes place, which can be expressed summarily as $\text{Cu}^{3+} + \text{Zn}^+ \rightarrow \text{Cu}^{2+} + \text{Zn}^{2+}$. At the same time the concentration of zinc oxide vacancies is lowered by interaction with the removed oxygen. Recombination of the majority carriers — positive holes with the formed electrons — causes a lowering of the p-type semiconductivity of the copper oxide. According to the electronic theory, an admixture of

a negative semiconductor causes a shift of the Fermi level on the oxide surface toward the conductivity band and thus lowers its adsorptivity with respect to a donor substrate¹⁵. Under the assumption that the mentioned phenomena will be rate-determining, the reduction rate will decrease with increasing content of zinc oxide. These conclusions are in accord with the results of a study of the reduction of nickel oxide and the p, n type semiconductive nickel oxide–zinc oxide system¹². With pure nickel oxide, it was proved experimentally that an increase in its stoichiometry leads by itself to a drop in its reduction rate regardless of the processes by which the stoichiometry was achieved^{6,12} (preparation conditions, thermal desorption of superstoichiometric oxygen, incorporation of ZnO, etc.). With the nickel oxide, zinc oxide system a drop in the reaction rate was observed with increasing content of zinc oxide¹². An exponential decrease of the reaction rate with increasing concentration of zinc oxide was found in the region where this system forms a homogeneous solid solution (up to 30 mol.% ZnO) and where the mutual influencing of the electronic structures is strongest. In the region of coexistence of two phases, but in direct contact conditioned by the method of preparation of the mixture, the dependence of the reaction rate on the composition showed a similar character as with the copper oxide–zinc oxide system (Fig. 3). This analogy shows that the mutual influencing of the both components can be expected even outside the region of the solid solution, where the system is also not equivalent to a mechanical mixture. This fact is substantiated by the results of reoxidation experiments. The primary reduction leads to a decrease of the high degree of mutual interaction of both components and after a subsequent oxidation a system results, where the nascent copper oxide with an unstable structure is secondarily reduced at a high rate.

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