MICROSTRUCTURE OF SOME OXIDE CATALYSTS

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When investigating two-component catalysts, some structural properties of two-component oxide catalysts (nonreduced and reduced) composed of nickel and zinc oxides as well as nickel and cobalt oxides, having varying content of both basic components, have been examined. Some samples were prepared from various starting materials (nitrates, carbonates) some of them were irradiated by a neutron Ra–Be generator. It was established that both the temperature of calcination employed and ionizing radiation applied, are of little effect on structural properties of the systems investigated. In all the systems consisting of nickel and zinc oxides, formation of solid solution of cubic structure, which is accompanied by occurrence of microstress in the sample, may be observed in the region of $0-30$ mol% of ZnO. Reduction of this system leads, in addition to metallic nickel, probably also to cubic alloy Ni–Zn and to an alloy of both metals, having a structure not yet established more closely. During preparation of the system consisting of nickel and cobalt oxides, primarily the spinel structure $CoO.Co_2O_3$ is produced, in addition to the NiO phase. Moreover, also a more complicated, but up to now not more closely determined structural type is produced. In the reduced nickel–cobalt system, formation of a substitutional nickel–cobalt solution with disordered substitution within total concentration range of $0-100\%$ was proved. With samples of a higher cobalt content also a hexagonal cobalt phase can be observed.

It is well-known[1] that catalytic properties of catalysts are in many cases influenced, among other things, by their microstructure. This aspect becomes important particularly with multicomponent catalysts, where influence of individual components between one another can be expected[2]. In the present paper, microstructure of a two-component catalyst consisting of nickel and zinc oxides, having varying content of both components, has been studied. The catalyst was prepared by coprecipitation of carbonates of both metals and also by calcination of nitrates of these metals. Likewise, the system of nickel and zinc oxides of the carbonate "origin", after irradiation by a neutron generator, has been studied. An attention has been also paid to the two-component catalyst consisting of nickel and cobalt oxides. All these systems have been studied also after their reduction with hydrogen.

EXPERIMENTAL

Preparation of samples. As starting substances for preparation of samples, nickel nitrate, zinc nitrate, cobaltous nitrate, and potassium carbonate, of A. R. purity, were employed. Condi-

tions for precipitation and subsequent calcination of nickel and zinc carbonates as well as composition of individual samples have been presented in paper[3]. In addition to the conventional temperature of calcination, of 400°C, some samples were prepared at temperatures of 300, 600, and 800°C. A portion of samples thus prepared was irradiated by a Ra–Be neutron generator having fluencies of thermal and epithermal neutrons of $2 \cdot 2 . 10^{11}$ and $8 \cdot 8 . 10^9$ n/cm^2, respectively. Total absorbed dose of γ-radiation amounted to $2 \cdot 1 . 10^{18}$ eV/g. The preparation of NiO–ZnO catalysts from nitrates, and their composition has been presented in another paper[4], and preparation as well as composition of samples of nickel and cobalt oxides have been described in paper[5]. In contrast to samples of the former oxides, the NiO–CoO samples were calcinated in a nitrogen atmosphere. After the preparation, the samples were let to stand in air at room temperature for several months. Afterwards, the X-ray analysis of them was made. All the samples were reduced at 400°C (3 h) in a stream of hydrogen. After cooling them under a hydrogen atmosphere, their structure was examined.

Technique of measurements. The modified Debye-Scherrer method was employed to study microstructure of the samples. The X-ray apparatus Mikrometa I was used. The copper anode tube was employed for the NiO–ZnO system, whereas for the NiO–CoO one, the iron anode tube was used. The tube was operated at a voltage of 30 kV and current of 12—24 mA. Selective reflections were detected on a X-ray film ORWO having two-sided emulsion. An exposure (15—30 min) was made for two positions of the sample with respect to the primary ray (angle between the sample plane and the primary ray was 30° and 60°).

RESULTS AND DISCUSSION

System NiO–ZnO

Investigation of this system showed all the samples examined to be the same from the structural point of view. For all of them, selective reflections only were found, originating from basic components of the system. The fact that irradiation of the samples by neutrons does not provide structural changes, may be accounted for a relatively low fluency of neutrons, to which the samples were exposed[6,7]. It has been also proved that neither the temperature of calcination within 300—400°C has an essential effect on the overall structure of the system studied. As has been shown, when measuring lattice parameter of cubic structure by the reversed ray method, this quantity rises for all the systems (carbonate, nitrate, irradiated) with the increasing zinc oxide content in the sample approximately up to 30 mol% of ZnO (Fig. 1). Maximum increase of this quantity amounts to about 0·62% of the original values. This gives prove of the fact that in the given region of compositions, a solid solution of zinc oxide in nickel oxide is produced, the cubic structure being maintained. A similar finding was made with the same system prepared under other conditions[9-11]. The fact that doublets cannot be resolved by reflection $K\alpha_1$ and $K\alpha_2$ in the X-ray patterns of the samples for which the solid NiO–ZnO solution can be anticipated, suggests that formation of the solid solution is accompanied by a rise of microstress in the system, which, as was proved, can be removed by heating the sample to a higher temperature.

The cubic structure lattice constant was established also for sample No 6 (39·6 mol% of ZnO, $a = 4·2067$ Å) which was after 1 hour's reduction by hydrogen at 400°C reoxidized in air at 400°C for 2 hours. The value found was equal to 4·1877 Å. When comparing the above-given value for the untreated sample with that of pure nickel oxide (sample 1, $a = 4·1775$ Å) it can be stated that the cubic structure parameter after reoxidation approaches that of pure NiO. On the basis of what has been said here it can be assumed that a longer time contact of both oxides is probably necessary for the formation of a saturated solid solution.

Magnitude of the cubic structure lattice parameter has been also studied as dependent on temperature of treating the samples within 150−1000°C for 1 hour

Fig. 1

Dependence of Parameter a [Å] of NiO Lattice upon Composition of NiO–ZnO (Carbonate) System Nonaffected by Radiation (●), Irradiated (○), and of Nitrate Origin (◑)
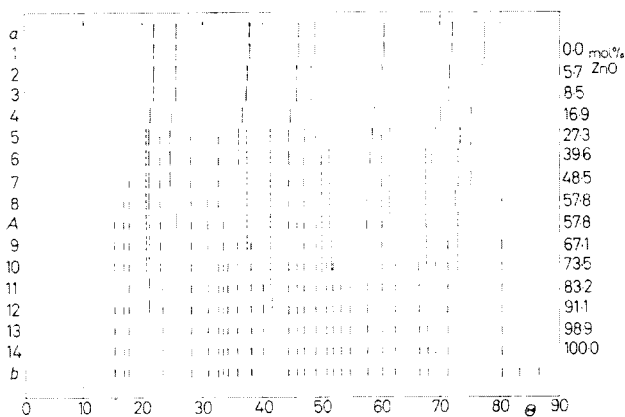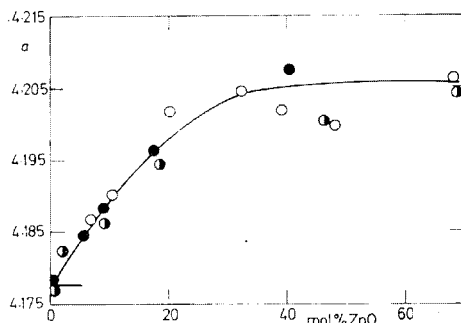——— Tabulated value of the parameter[8].

Fig. 2

Schematic Diagram of Debye Patterns of a System of Reduced Samples (Ni–ZnO) of Carbonate "Origin"

a Tabulated reflections of Ni, b tabulated reflections of ZnO, A sample calcinated at 600°C. Long abscissas denote reflections of Ni, short abscissas reflections of ZnO, broken abscissas denote reflections of a new structure.

TABLE I

Lattice Parameter of Cubic Structure [Å] of Some NiO–ZnO Samples Thermally Treated under Different Conditions

No	ZnO mol %	a, Å		
		—	500°C	1 000°C
1	0·0	4·1775	4·1774	—
6	39·6	4·2067	4·1942	—
5[a]	47·0	4·1992	4·1934	4·2090

[a] Sample by generator of neutrons irradiated.

in a nitrogen atmosphere (Table I). It was established that only a temperature of 500°C will affect magnitude of the examined parameter towards lower values only for the samples consisting of both oxides (irrespective of the fact whether they were irradiated
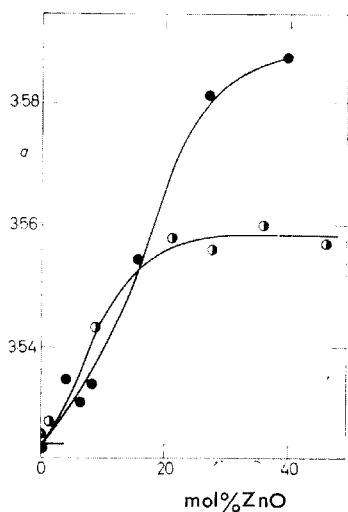

FIG. 3

Dependence of Parameter a [Å] of Ni Lattice upon Original Composition of the NiO–ZnO System of "Carbonate" (●) and "Nitrate" (◑) Origins
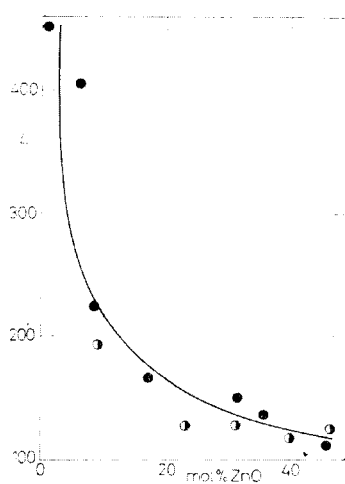
———— Tabulated value.

FIG. 4

Dependence of Magnitude of Coherent Regions of Reduced Nickel L [Å] upon Composition of the Ni–ZnO System for Samples Prepared from Carbonates (●) and Nitrates (◑)

beforehand). This may occur as a result of a change in the oxygen tension of samples, caused by the heat treatment. The fact that this effect does not occur with pure nickel oxide is obviously connected with the fact that, as has been experimentally confirmed, zinc oxide affects to a great extent affinity of nickel oxide to oxygen. On the other hand, however, higher temperature of the treatment $(1000°C)$ obviously stimulates formation of a solid solution, similarly as was observed in the system of nickel and manganese oxides[12]. Contrary to the region with surplus of nickel oxide up to 40 mol% of NiO, no change in parameters of zinc oxide in any series of this system takes place.

System NiO–ZnO after Reduction

As evident from Fig. 2, this system is predominantly composed of cubic nickel structure and hexagonal zinc oxide structure. In addition, reflections, which belong

TABLE II

Dependence of Parameter a (NiO) upon Composition of $NiO-Co_3O_4$ Samples

No	mol% Co_3O_4	a(NiO), Å
1	0·0	4·1754
2	0·5	4·1753
3	1·9	4·1772
4	10·0	4·1824
5	19·7	4·1887

TABLE III

Dependence of Parameter a (Co_3O_4) upon Composition of $NiO-Co_3O_4$ Samples

No	mol% NiO	a(Co_3O_4), Å
16	0·0	8·083
12	11·6	8·083
10	29·9	8·079
9	40·0	8·075
8	50·5	8·070

to none of the basic structures of the system, occur here in the region of mean concentration. This holds for all three studied series of the system. This character is not changed either by a higher temperature of calcination of the sample (sample A). It can be said that under given conditions, total reduction of nickel oxide takes place. This system differs thus from an analogous system prepared by calcination of hydroxides[13], where complete reduction of the oxide occurred only in the course of the dehydrogenation reaction, which was accompanied by "splitting" of lines of the cubic nickel structure. This effect was explained by the authors by a partial reduction of zinc oxide and by formation of cubic alloy NiZn.

Owing to the fact that in our case, the increase of the cubic structure parameter (with the increasing amount of zinc oxide in the sample up to 30 mol% of ZnO (Fig. 3)) by 1·6% for the "carbonate" system and by 0·96% for the "nitrate" system was even here observed, it can be assumed that formation of cubic Ni–Zn alloy is here involved. This is proved 1 kewise by the fact that the found parameters of the
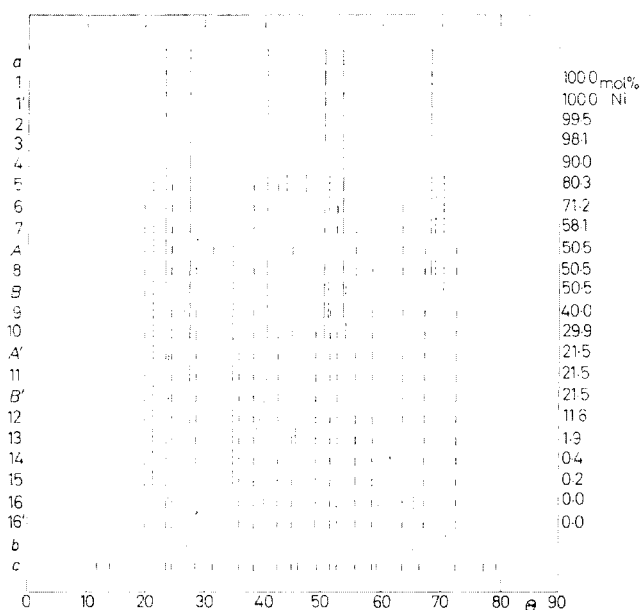

FIG. 5

Schematic Diagram of Debye-Patterns of Samples of the NiO–CoO System

a Tabulated reflections of NiO, *b* tabulated reflections of CoO, *c* tabulated reflections of Co_3O_4, 1′,16′ samples calcinated in air. Samples A,A′ calcinated at 200°C, B,B′ calcinated at 800°C. Long abscissas NiO reflections, short abscissas Co_3O_4 reflections, short broken abscissas CoO reflections, long broken abscissas reflections of a new structure.

solution, amounting to $3 \cdot 524 - 3 \cdot 588$ Å (as dependent upon composition) are in good agreement with tabulated values $(3 \cdot 520 - 3 \cdot 588$ Å$)^{13,14}$. Moreover, the fact that during the reduction a partial reduction of zinc oxide is involved, was directly confirmed by gravimetric study of the process of reduction. It is evident from Fig. 3 that formation of this alloy is to a great extent influenced by character of the starting substances employed in the preparation of oxides. Thus, also the mentioned diverse behaviour of the system prepared from hydroxides may be explained[13]. The process of reduction in our case likely leads to a more complicated system which becomes evident by further selective reflections (Fig. 2). It is possible that the Ni–Zn alloy is again involved, but of another character, since this system can crystallize in various modifications some of them being not sufficiently up to now examined[14]. As has been further shown by measuring half-width using nickel reflections (313) and (024) (Fig. 4), size of reduced nickel particles decreases with the increasing zinc oxide content, irrespective of the sample "origin". This effect, which was also observed by Rubinštejn, can be explained by the fact that dispersity of the produced nickel is within the reduction
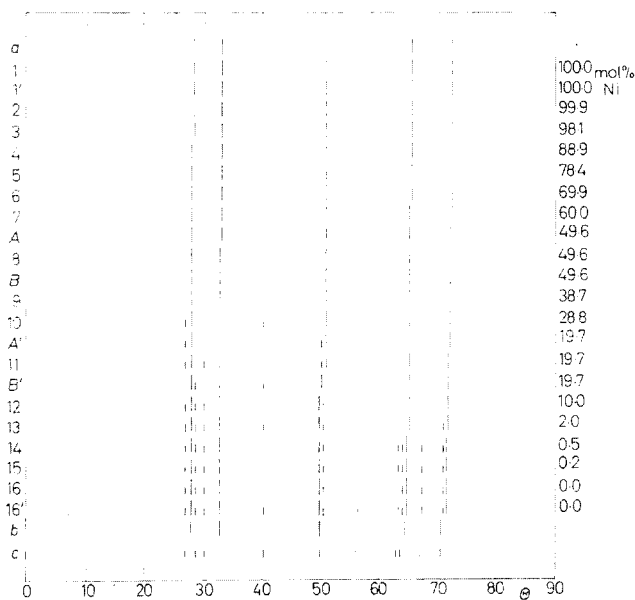

Fig. 6

Schematic Diagram of Debye Patterns of Reduced Samples of the Ni–Co System

a Tabulated reflections of Ni, *b* tabulated reflections of Co (cubic), *c* tabulated reflections of Co (hexagonal), long abscissas reflections of Ni and cubic Co, short abscissas reflections of hexagonal Co. Symbols 1′,16′, A,B, A′,B′, have equal meaning as in Fig. 5.

process to a great extent influenced by the zinc oxide (or partial reduced zinc) present. In the second edge region of this system (surplus of ZnO) it has been established that parameters of the hexagonal phase do not change with the nickel content of the sample.

System NiO–CoO

The Debye patterns of samples of this system with varying content of both components are graphically presented in Fig. 5. It is evident that this system consists predominantly of cubic structure of nickel oxide and spinel structure of Co_3O_4, which was demonstrated earlier when studying stage and kinetics of the reduction of the samples[5]. The structure of simple cobaltous oxide can be observed only with pure cobaltous oxide which was calcinated in nitrogen (sample No 16), and with the sample of higher cobalt content calcinated at 800°C (sample B'). Otherwise, the temperature of calcination has no essential effect on the structure of the samples.

In addition to the structure of appropriate NiO, Co_3O_4, and CoO, further reflections of a phase, up to now not closely examined, can be observed, which may be ascribed to a compound denoted by a summary symbol Co_{3-x}—Ni_xO_4. An analogous compound was namely observed in the system of zinc and cobaltous oxides[15]. A direct proof of this assumption will require a further, more detailed study of this system.

Similarly as in the NiO–ZnO system, also here in the region with excessive nickel oxide in the sample, its parameter increases with the increasing amount of cobalt oxide (Table II). The change examined, however, is smaller than in the NiO–ZnO system. A similar influence of both components can be with this system observed in the second edge region (Table III), where the parameter of spinel decreases with the increasing nickel oxide amount. It can be then assumed that in both edge regions a solid solution can be produced under suitable conditions.

System NiO–CoO after Reduction

The Debye patterns of samples consisting of nickel and cobalt oxides after reduction are graphically presented in Fig. 6. From this Figure it follows that the system is composed of nickel and cobalt having cubic structures, and with samples of a higher cobalt content, likewise cobalt crystallizing in the hexagonal system occurs. It can be at the same time pointed out that temperature of the preparation of oxides and atmosphere of calcination has no substantial effect upon structure of the system under reduction. In spite of the fact that at temperatures lower than 480°C cobalt crystallizes in the hexagonal system[14], the presence of cubic cobalt in our system can be accounted for the stabilizing effect of hydrogen by means of which the samples were reduced[16]. This stabilization is obviously insufficient and for that reason, a part of cobalt crystallizes in the hexagonal system.

Fig. 6 shows that the cubic structure constant congruently changes from a value of one pure component to a value of the second component. This was directly confirmed in the study of samples using the reversed ray method, where linear dependence of parameter of this structure upon composition over the concentration range of $0-100\%$ was found. This dependence gives evidence of the substitution solution of both metals, which has been described formerly[14]. Since in the patterns no other reflections of possible hyperstructure can be seen, a solution of disordered substitution is most likely involved.

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