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Effect of Mechanochemical Activation on the Catalytic Properties of Zinc Oxide

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Abstract—The reasons for changes in catalytic activity as a function of the time of mechanochemical activation in a planetary mill were studied with the use of a set of physicochemical techniques. The dependence of the specific rate of CO oxidation on the time of mechanochemical activation exhibited an extremal character. Small-angle interblock boundaries, disordered dislocations, and shear defects were formed in the sample with maximum activity because of mechanochemical activation. The linear dependence of the specific rate of CO oxidation on the value of microstresses suggested that the above defects were responsible for an increase in the catalytic activity. It is likely that oxygen atoms situated at the sites of the outcrop of defects on the surface served as elementary active centers.

INTRODUCTION

The question of whether crystal structure defects are catalytically active centers has long been under discussion. The supporters of this hypothesis advance many arguments, although all of them are only indirectly relevant. A great number of such publications were cited in the review [1]. It is our opinion that the linear dependence of specific catalytic activity on the concentration of defects of a particular type would be strong and unambiguous evidence for the above hypothesis. Methods for the correct determination of specific catalytic activity were developed and implemented. However, the determination of the nature and concentration of crystal structure defects is an extremely complicated problem even for state-of-the-art physicochemical techniques. This complicated problem is aggravated by the occurrence of several types of defects; in this case, it is much more difficult to distinguish the effect of a particular type on catalytic activity. As a rule, researchers face this situation in the studies of defect systems prepared with the use of traditional chemical methods. These objective difficulties are responsible for an extremely small number of publications in which correlations between specific catalytic activity and concentration of defects of a certain type were obtained. In turn, for this reason, general conclusions on the nature of the effect of crystal structure defects on catalytic activity cannot be made. At this stage, it is our opinion that information on the nature of this effect in various objects should be accumulated.

To facilitate the solution of this problem, we used mechanochemical activation for the generation of defect structures. The advantages of this technique consist in the induction of crystal structure defects in high concentrations and the preferred generation of defects of one type or, in some cases, of only one type [2]. This considerably facilitates the identification of the nature and the determination of the concentration of defects.

In this work, we demonstrate the effectiveness of the described approach using zinc oxide as an example. Published data on the effect of mechanical treatment on the catalytic properties of ZnO are available. It was found that the catalytic activity of ZnO in the reactions of hydrogen peroxide decomposition and isopropanol photooxidation decreased with increasing time of treatment in a ball mill [3, 4] and linearly depended on the degree of disordering of the crystal lattice [4]. Sadahiro [5] studied the effect of the mechanical treatment of ZnO on the activation energy of H_2O_2 decomposition and found that the activation energy decreased with decreasing particle size and increased proportionally. Sadahiro attempted to determine the nature of defects induced by mechanical treatment and to relate the catalytic properties of mechanically activated samples to the occurrence of different types of defects [6, 7]. Two types of paramagnetic defects were detected, for which the activation energy of the reaction of H_2O_2 decomposition decreased with increasing EPR signal intensity [6]. Sadahiro attributed these signals to screw dislocations and compression distortions of the crystal lattice. More recently, Sadahiro assumed that broken bonds in zinc oxide are catalytically active sites [7]. In all of the cited publications, imperfect methods were used for determining catalytic activity. Thus, the use of activation energy as a measure of catalytic activity [6, 7] cannot be considered as appropriate; the relation of an integrated value such as conversion to sample surface areas [3, 4] can also lead to incorrect conclusions.

Previously, we attempted to study the structure and morphology characteristics of zinc oxide after mechanochemical activation [8]. However, the low sensitivity of applied techniques and the absence of effective procedures for studying the defect structure of powder materials did not allow us to obtain information on the most interesting region of short activation times, where a maximum catalytic activity was observed. The development of advanced instruments and experimental techniques allowed us to return to studies of mechanically activated zinc oxide.

EXPERIMENTAL

The samples of ZnO were subjected to mechanochemical activation in an EI 2 × 150 centrifugal planetary mill with steel balls 5 mm in diameter in stainless-steel drums. The weights of the balls and a sample were 200 and 5 g, respectively; the drum speed was 11 s^{-1}. In a number of cases, the samples were activated in an AGO-2 centrifugal planetary mill in ceramic drums with corundum balls, as well as in a quartz vibrating mill at a frequency of 50 Hz and an amplitude of 5 mm or in a Dezi 1A41 disintegrator with six-row rotors at a rotating speed of 250 s^{-1}.

The catalytic activity of the samples in CO oxidation was evaluated as the reaction rate on a unit surface area basis. The reaction rate was determined under gradientless conditions in a flow-circulation unit at 570–670 K; the catalyst weight was 5 g; the flow rates of CO and air were 2.25 and 5 l/h, respectively (the CO/O_2 molar ratio was 2).

The specific surface area was determined by the thermal desorption of argon.

Because the broadening of diffraction peaks was very small at the first stages of mechanochemical activation, the diffraction experiment was performed at the Station of Synchrotron Radiation at the Budker Institute of Nuclear Physics, Siberian Division, Russian Academy of Sciences (Novosibirsk) in order to reliably determine this broadening. The high-resolution diffractometer provided an instrumental diffraction peak width from 0.05° to 0.08° in the angle region 30°–130° (2Θ), which is much smaller than that of production diffractometers. Moreover, with the use of synchrotron radiation, the problem of separating doublet peaks does not appear, as with commonly used CuK_α radiation.

The electron micrographs were obtained on a JEM-2010 electron microscope with an accelerating voltage of 200 kV and a resolving power of 0.14 nm.

The *in situ* EPR studies of the samples were performed with the use of an ERS-221 EPR spectrometer as described elsewhere [9]. The mechanical activation of zinc oxide was performed in air; next, the sample was placed in an ampoule for EPR measurements. If necessary, the ampoule was attached to a vacuum unit for performing experiments under conditions of a controlled gas phase. Note that in all cases the use of steel equipment resulted in the appearance of a broad line in the EPR spectra ($\Delta H > 1000$ G), which is characteristic of a ferromagnetic impurity phase. The concentration of this phase increased with increasing time of treatment; however, the appearance of this phase had practically no effect on the character and properties of bulk defects formed in zinc oxide upon mechanical activation, which will be considered below. This was demonstrated by comparative studies of samples prepared in steel and ceramic drums.

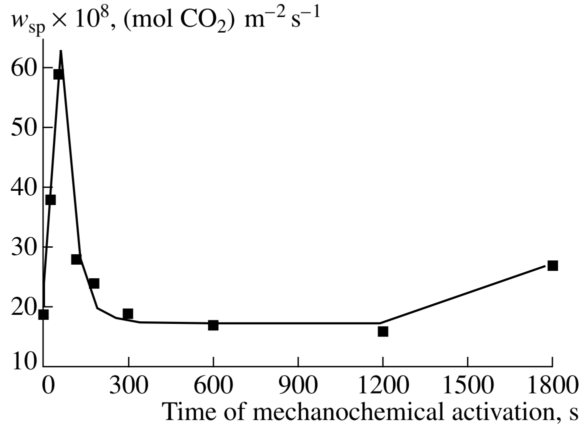

Fig. 1. Dependence of the specific rate of CO oxidation (w_{sp}) on the time of mechanochemical activation of ZnO.

The surface of mechanically activated ZnO samples was studied by X-ray photoelectron spectroscopy (XPS). The studies were performed on a VGESCALAB electron spectrometer. For the excitation of electrons, MgK_α radiation was used. The samples were applied to nickel gauze by rubbing. The spectra were measured in a deceleration mode with a constant energy of electron transmission through the analyzer equal to 20 eV. The pressure in the spectrometer chamber was no higher than 10^{-7} Pa. The heating of the samples in an atmosphere of oxygen was performed immediately in the spectrometer chamber at an oxygen pressure of 10^{-3} Pa. The spectra were measured under the same conditions. The samples were placed in the spectrometer chamber immediately after mechanochemical activation at a minimum contact time with the atmosphere. The materials of planetary mill drums and balls (Fe, Ni, and Cr) were not detected in the test samples with the use of XPS spectra.

RESULTS AND DISCUSSION

Catalytic Properties

The treatment of ZnO samples in a vibrating mill for 0.5–8 h did not change the catalytic activity in CO oxidation. At the same time, the treatment in planetary mills significantly affected the specific catalytic activity. At short activation times (τ = 30–60 s), a dramatic increase in the specific rate of CO oxidation was observed (Fig. 1). During the subsequent activation for 120–300 s, a sharp decrease in the activity to the level of the parent sample was observed, and the activity

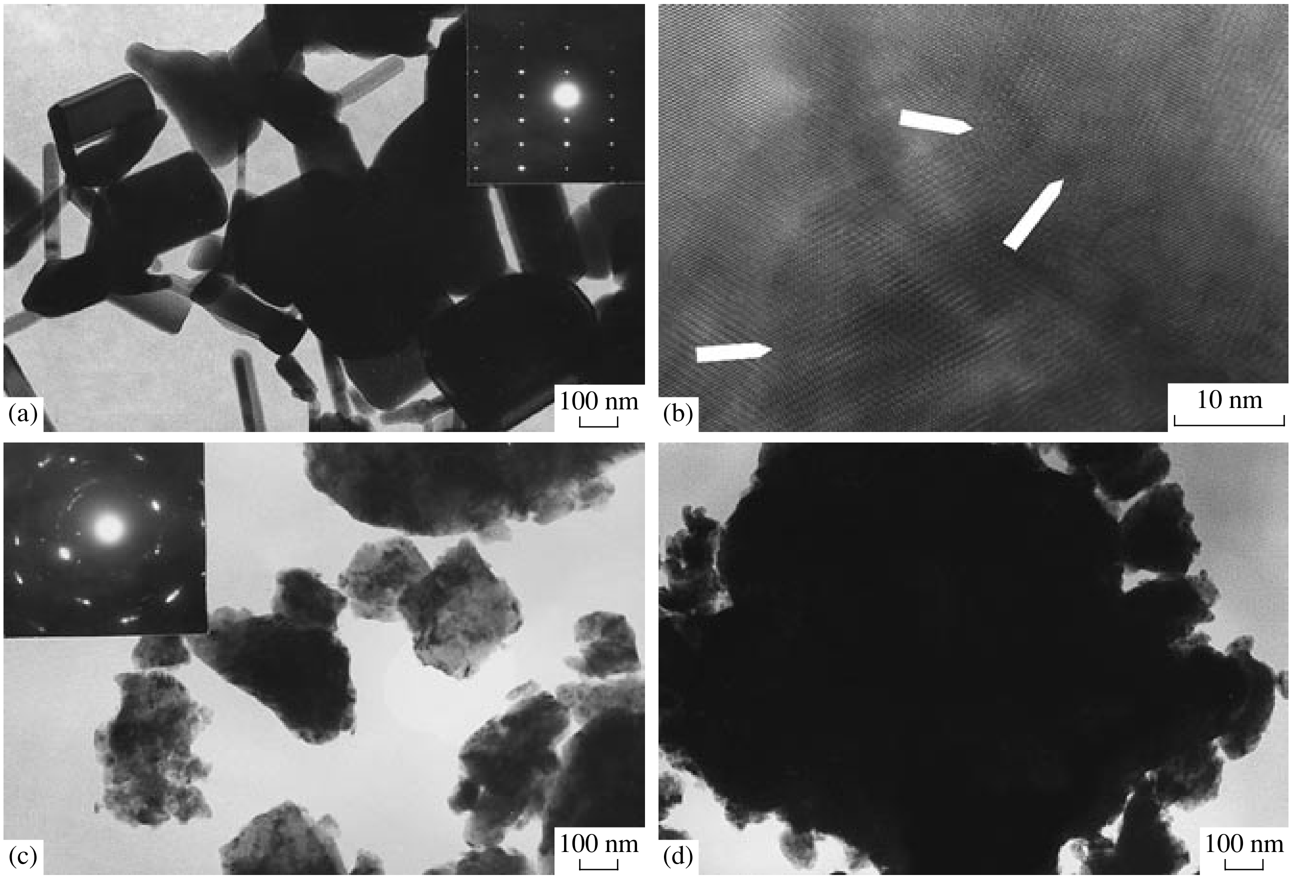

Fig. 2. Electron micrographs of ZnO samples: (a) the parent sample and (b–d) samples mechanically activated for 60, 600, and 1800 s, respectively.

somewhat increased at an activation time of 1800 s. The increase in the specific catalytic activity could be explained by the occurrence of metals in the samples because of abrasion from balls and drum walls. However, chemical analysis demonstrated that the metal content linearly increased with time of mechanochemical activation, whereas the dependence of activity on time of mechanochemical activation exhibited a complex character. Moreover, the form of the dependence remained qualitatively unchanged upon the activation of samples in ceramic drums with corundum balls. To determine the reason for this change in the catalytic properties, it was necessary to reveal which changes occurred in the crystal structure of zinc oxide in the course of mechanochemical activation.

Electron Microscopic Data

From the electron-microscopic data, it follows that the parent sample consisted of platelike particles of size 0.3–0.5 μm (Fig. 2a). The structure of the particles was well ordered; microdistortions were practically absent. Each particle gave a point electron-diffraction pattern with sharp reflections (Fig. 2a), which suggests the absence of microblocks.

In the first 30–60 s of mechanochemical activation, microdistortions appeared in the particles, and interblock boundaries (mainly small-angle) were formed, which are indicated with arrows in Fig. 2b. In this case, the physical size of particles remained unchanged. Mechanochemical activation for 600 s resulted in the dispersion of zinc oxide crystals with the formation of particles of size 0.05 μm (Fig. 2c). The microdiffraction of these particles represents a set of ring reflections, which are characteristic of a polycrystalline material (Fig. 2c). Upon a longer mechanochemical activation, the aggregation of small particles to agglomerates of size greater than 1 μm occurred (Fig. 2d). The constituent particles of the agglomerates exhibited microdistortions.

X-ray Diffraction Data

A study of the dependence of the halfwidths of diffraction peaks on the angle of reflection demonstrated that the peak broadening of the parent sample, as compared with that of a reference sample of corundum, can be interpreted as a size effect from particles of size 0.3–0.5 μm, which corresponds to electron-microscopic data. Mechanochemical activation resulted in an anisotropic broadening of diffraction peaks: peaks with *00l* indices broadened to a much lesser extent as compared with reflections of other types (Table 1).

For more clarity, we graphically illustrate these results. Figure 3 demonstrates the dependence of the broadening of diffraction peaks on the angle of diffraction. It can be clearly seen in Fig. 3 that the broadening of peaks with *00l* indices was much smaller than the broadening of other lines.

Both the anisotropy of the resulting coherent-scattering regions and the occurrence of stacking faults can be responsible for anisotropic line broadening. According to electron-microscopic data, the samples with an activation time of 30–60 s did not exhibit a noticeable number of stacking faults; however, a microblock structure of particles primarily with small-angle interblock boundaries was formed. To demonstrate that the anisotropy of diffraction peak broadening was due to the anisotropic form of coherent-scattering regions, we used an original program for calculating theoretical diffraction patterns. This program allowed us to simulate powder diffraction patterns for both anisotropically shaped crystallites and crystals with high concentrations of stacking faults [10].

Figure 4a demonstrates fragments of the diffraction pattern of a sample subjected to mechanochemical activation for 60 s and a theoretical diffraction pattern calculated for cylindrically shaped particles 100 nm in diameter and 25 nm in height. In general, the model X-ray diffraction pattern was consistent with the experimental pattern. The *R* factor for this model was 6%.

The second model implied that the sample has stacking faults. In this case, we calculated that the concentration of stacking faults of no smaller than 0.01 should be introduced into the model to adequately describe the broadening anisotropy of diffraction peaks with *100*, *002*, and *101* indices (Fig. 4b). However, the broadening of a 102 peak should occur at this concentration of faults, but this was not observed experimentally. The minimum possible *R* factor for this model is 22%, which is much worse that in the first model.

The occurrence of diffraction peaks of several orders of diffraction *00l* and *h00* provides an opportunity to evaluate not only the size of coherent-scattering regions in corresponding crystallographic directions but also the value of structure microdistortions (Table 2). The value of microdistortions, as well as catalytic activity, is an extremal function of the time of mechanochemical activation with a maximum at an activation time of 60 s. Data in Table 2 suggest that the microdistortions are due to both the appearance of small-angle interblock boundaries and the formation of other defects. The former follows from a decrease in coherent-scattering regions for *kh0* directions with a simultaneous increase in the value of microdistortions for a sample activated for 30 s. As the time of mechanochemical activation was increased to 60 s, the size of coherent-scattering regions remained unchanged, whereas the value of microstresses increased. This increase was most likely due to the appearance of nonassociated dislocations and the displacement and turn of oxygen layers over distances shorter than those required for the formation of stacking faults. In our opinion, the latter assumption is more probable because a dramatic decrease in the value of microdistortions was observed simultaneously with fracturing and crystal dispersion processes in accordance with electron-microscopic data. Because changes in the value of microdistortions are analogous to changes in specific catalytic activity, it is believed that an increase in the activity is due to the appearance of the following defects: small-angle inter-

Table 1. Diffraction peak broadening in ZnO samples

hkl	2Θ, deg (λ = 1.5345 Å)	Experimental broadening *B*(2Θ), deg			Instrumental broadening *b*(2Θ), deg
		Mechanochemical activation time, s			
		0	30	60	
100	31.63	0.070	0.110	0.120	0.050
002	34.28	0.060	0.080	0.085	0.050
101	36.10	0.070	0.120	0.140	0.055
102	47.34	0.065	0.130	0.150	0.055
110	56.35	0.065	0.135	0.170	0.055
200	66.09	0.080	0.135	0.175	0.055
004	72.25	0.075	0.120	0.135	0.060
202	76.62	0.090	0.175	0.230	0.060
300	109.75	0.130	0.230	0.310	0.065
006	124.30	0.145	0.245	0.310	0.080

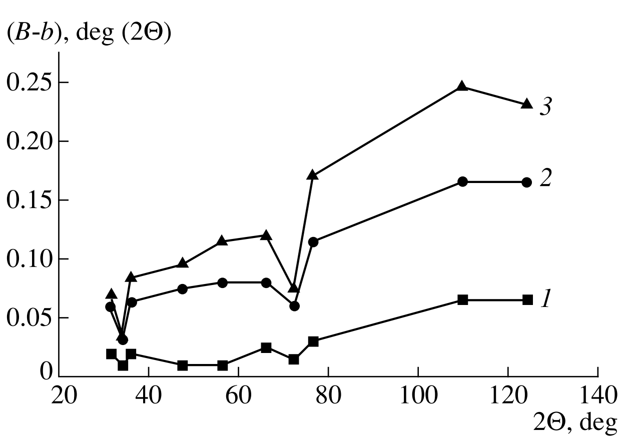

Fig. 3. Dependence of the broadening of diffraction peaks on diffraction angle for (*1*) the parent sample and samples activated for (*2*) 30 and (*3*) 60 s.

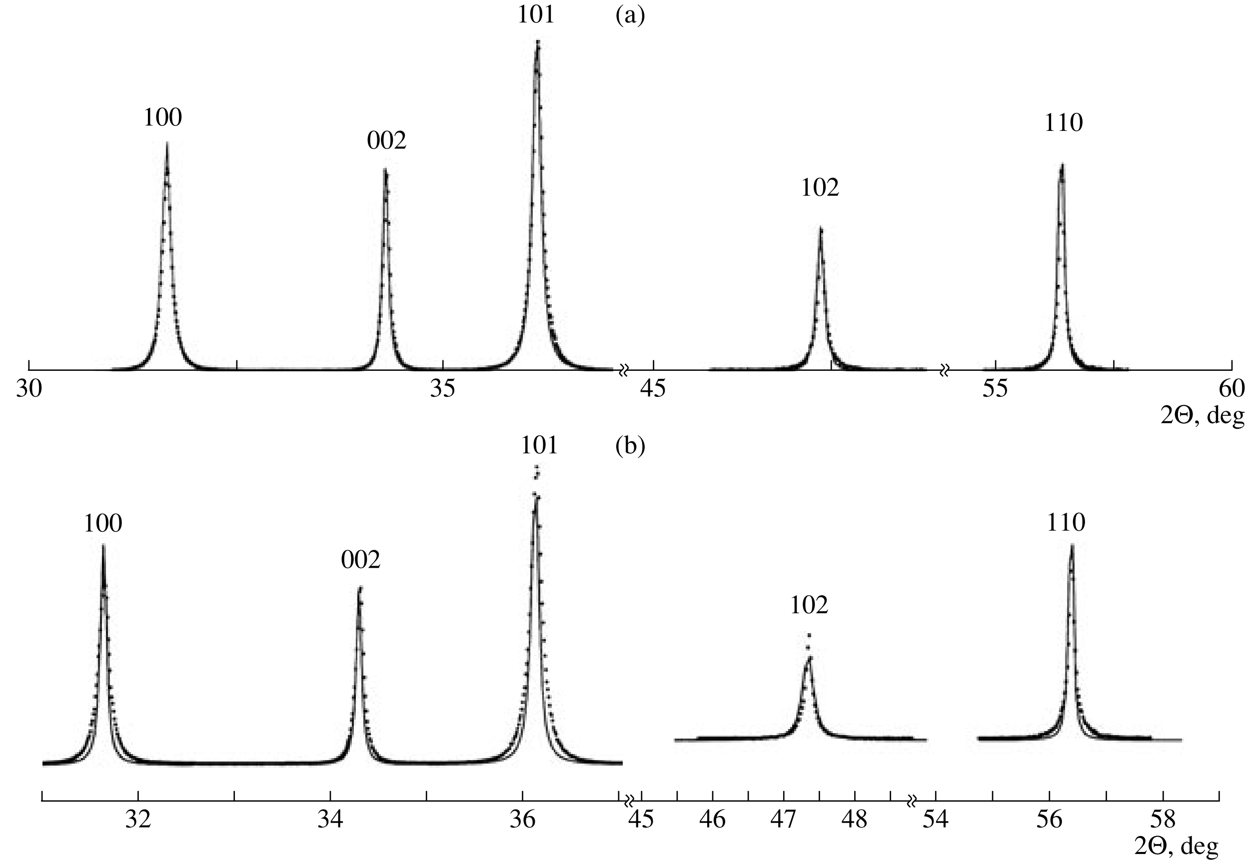

Fig. 4. Comparison between experimental (points) and theoretical (solid lines) diffraction patterns for models that imply (a) small-angle boundaries and (b) stacking faults.

block boundaries (dislocation associates), disordered dislocations, and the displacements and turns of layers.

Thus, at short times of mechanochemical activation, crystal structure microdistortions appeared in zinc oxide and anisotropically shaped microblocks with small-angle boundaries between them were formed. In this case, the primary particles of zinc oxide were practically not divided into smaller coherent-scattering regions transversely to the direction *C*. In this direction, only variations in interplanar spacings (microdistortions) were observed. At the same time, interblock boundaries developed parallel to this direction to result in more pronounced broadening of *h00*, *hk0*, and *hkl* reflections. Figure 5 schematically illustrates the structure deformation of zinc oxide at the early stage of mechanochemical activation.

Table 2. Dependence of the size of coherent-scattering regions (D) and the value of microdistortions (ε) for various crystallographic directions on the time of mechanochemical activation

Mechanochemical activation time, s	D_{00l}, nm	$\varepsilon_{00l} \times 10^4$	D_{hk0}, nm	$\varepsilon_{hk0} \times 10^4$
0	≥250	–	≥250	–
30	≥250	2.0	100	3.0
60	≥250	5.5	110	5.0
120	42	1.0	35	0.6
300	35	1.5	25	<0.5

At the time of mechanochemical activation equal to 60 s, the value of microdistortions considerably increased, whereas the sizes of coherent-scattering regions remained practically unchanged. As the time of mechanochemical activation was increased to 120 s, the size of coherent-scattering regions dramatically decreased. However, electron-microscopic data and the measurements of specific surface areas (Table 3) demonstrated that these changes were not related to the dispersion of parent particles. This suggests that a microblock structure with coherent-scattering regions smaller than 50 nm was formed in the particles because of the relaxation of microdistortions that appeared in the structure at the preceding stage. In this case, the type of interblock boundaries was changed: great-angle interblock boundaries were formed.

EPR Data

EPR spectroscopy is an effective technique for studying mechanically activated substances [11, 12]. We applied this technique to study zinc oxide. The results of this study will be considered in more detail elsewhere; here, we only dwell on the results that allowed us to determine the nature of the effect of mechanochemical activation on catalytic activity.

Paramagnetic centers of four types were formed in ZnO upon mechanochemical activation in a vibrating mill and at very short treatment times in a planetary mill. Table 4 summarizes the parameters and the assignment of EPR signals to particular point defects.

Heating in air resulted in the annealing of the major portion of point defects. Thus, defects of the A and D types were annealed at 370–420 K; this fact is consistent with published data [7, 11]. However, a further increase in the temperature, along with a decrease in the concentration of centers B in the temperature region 520–570 K, was accompanied by the appearance of new centers of the E type with $g_\perp = 1.9970$ and $g_\parallel = 1.9900$ and an increase in the concentration of Zn^+ ions (centers of the C type) (Fig. 6) even on heating in an oxidizing atmosphere (in O_2 or air). The samples activated for a short time (30–60 s) exhibited a maximum number of these centers, whereas centers of the C type were not observed in a sample activated for 600 s after heating at 520–570 K. Note that the rates of formation of Zn^+ on sample treatment with CO and the rates of disappearance of these ions on treatment with oxygen were unusually high. This behavior of the system allowed us to assume that redox processes occurred at extended defects. There is a qualitative correlation between the amount of Zn^+ centers formed upon reduction and specific catalytic activity; however, we failed to obtain quantitative relationships because of a strong broadening of the spectra of Zn^+ due to the appearance of conduction electrons.

The experimental data suggest that oxygen exhibits high lability at the sites of crystal structure defects (it is most likely that these are small-angle interblock boundaries). Because of this, oxygen readily participates in the oxidation of CO with the formation of Zn^+ centers; then, it is easily regenerated under exposure to oxygen from a gas phase; that is, a stepwise mechanism occurs with the participation of oxygen bound to defects. Let us give another example of the high oxidizing ability of activated ZnO. The chemisorption of hydrogen selenide at room temperature on a sample activated for 60 s resulted in the oxidation of hydrogen selenide to elemental selenium. The occurrence of this reaction was not observed in a sample activated for 600 s, instead, usual chemisorption took place.

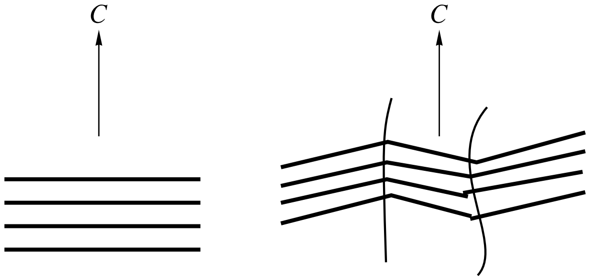

Fig. 5. Schematic diagram of the deformation of the crystal structure of ZnO at the initial stage of mechanochemical activation.

XPS Data

Because heterogeneous catalysis takes place at the surface of catalysts, information on changes in the state of the surface under mechanical action is of importance for understanding the nature of the effect of mechanochemical activation on catalytic properties. A study of the physicochemical properties of catalysts under reaction or near-reaction conditions is of paramount importance to the assignment of the nature of the active centers of catalysts. An XPS study of ZnO under conditions of the CO oxidation reaction at the molar ratio $CO/O_2 = 2$ is difficult to perform because the reduction of zinc oxide and the deposition of zinc metal on the walls of the spectrometer chamber occur on heating under high-vacuum conditions. Therefore, we studied the surface of ZnO samples on heating in a flow of O_2 at $P = 30^{-3}$ Pa. The chemical composition of the surface was monitored by measuring changes in the ratio between the integrated line intensities Zn 3*d*/Zn 2*p*, Zn 2*p*/O 1*s*, and Zn 3*d*/O 1*s*. The use of these ratios allowed us to obtain information on surface layers of different thickness because the electron free path essentially depends on the kinetic energy. Thus, the Zn 2*p*,

Table 3. Dependence of the specific surface area on the time of mechanochemical activation

Mechanochemical activation time, s	S_{sp}, m^2/g
0	6.0
30	6.3
60	6.8
120	7.0
180	6.7
300	6.8
600	10.0
1200	8.8
1800	7.4

Table 4. Parameters of the EPR spectra of mechanically activated ZnO

Type of paramagnetic centers	g-Factor	ΔH, G	Assignment
A	2.0031	–	Paired defects or their associates of the vacancy type
	2.0063	–	
	2.0081	–	
B	$g_{av} = 2.0136$	2.83	The nature is unclear
C	$g_{av} = 1.9576$	6.53	Two types of Zn^+
D	$g_{\perp} = 2.0196$	–	O^- radical anion
	$g_{\parallel} = 2.0032$	–	

O 1*s*, and Zn 3*d* lines provide information on surface layers 0.6–0.8, 1.5–2.0, and 2–3 nm in thickness, respectively [13, 14]. The surface enrichment in particular components or surface depletion can be monitored by comparing the above ratios under changes in the conditions of mechanochemical activation.

An analysis of changes in the Zn 2*p*/O 1*s* ratio (Fig. 7a) exhibited a strong difference between parent and activated samples. In a parent sample, this ratio decreased on heating in the range 300–500 K, whereas it increased at higher temperatures. In a sample activated for 600 s, only a decrease in the concentration of zinc with respect to oxygen was observed. Changes were insignificant in a sample activated for 60 s. A decrease in the Zn 2*p*/O 1*s* line intensity ratio and an increase in Zn 3*d*/Zn 2*p* in the sample activated for 60 s (Fig. 7) can be due to a surface shielding effect of elemental carbon, whose concentration increased on heating. In our opinion, this behavior of carbon is indicative of its segregation at the outcrop sites of defects. Diffusion pump oil, which arrived at the spectrometer chamber in insignificant amounts, can be the source of carbon. Among the samples studied by XPS, the sample activated for 60 s exhibited a maximum imperfection, whereas defects were absent from the sample activated for 600 s because the zinc oxide structure relaxed as a result of crystal dispersion on defects.

On heating in an oxygen atmosphere, changes in the Zn 3*d*/Zn 2*p* intensity ratio were essentially different in the parent and activated samples. In the parent sample, a decrease in the surface concentration of zinc, as compared with the bulk concentration, was observed in the range 300–500 K; in contrast, the surface zinc content increased at temperatures higher than 500 K (Fig. 7b). In the sample activated for 600 s, an increase in the Zn 3*d*/Zn 2*p* intensity ratio over the temperature range 300–500 K was observed to a smaller degree, whereas this ratio remained practically unchanged over the range 500–750 K. In the sample activated for 60 s, the value of Zn 3*d*/Zn 2*p* varied over a narrower range.

Along with the above changes, the O 1*s* spectra of the parent sample and the sample activated for 600 s exhibited an increase in the intensity of a peak with $E_b = 533$ eV, which is characteristic of low-coordinated oxygen, over the range 300–500 K. In the sample activated for 60 s, an increase in the intensity of this peak was insignificant. As the temperature was further increased, the intensities of peaks with $E_b = 533$ eV for the parent sample and the sample activated for 600 s decreased, whereas this peak remained in the spectrum of the sample mechanochemically activated for 60 s up to 770 K (Fig. 8).

Based on the above data, we suppose that a decrease in the surface concentration of zinc with respect to oxygen at temperatures lower than 500 K was due to an increase in surface coverage with adsorbed oxygen,

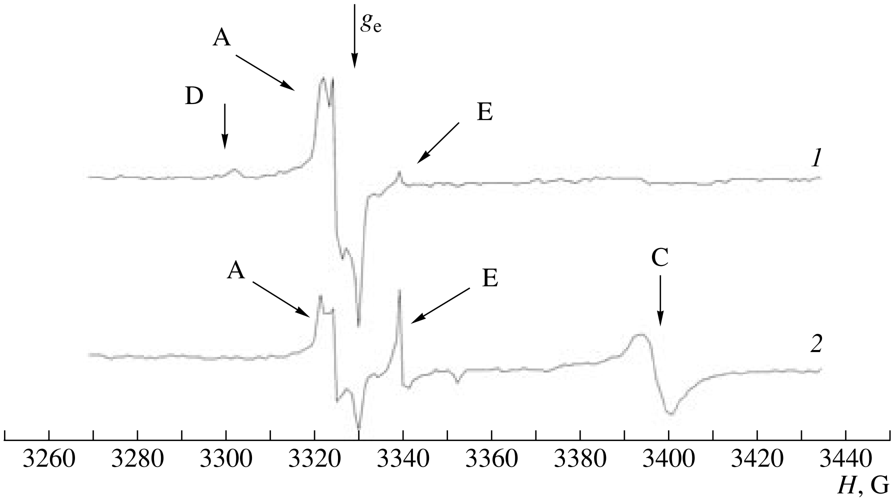

Fig. 6. EPR spectra of ZnO samples (*1*) after mechanochemical activation for 60 s and (*2*) the subsequent calcination at 520 K.

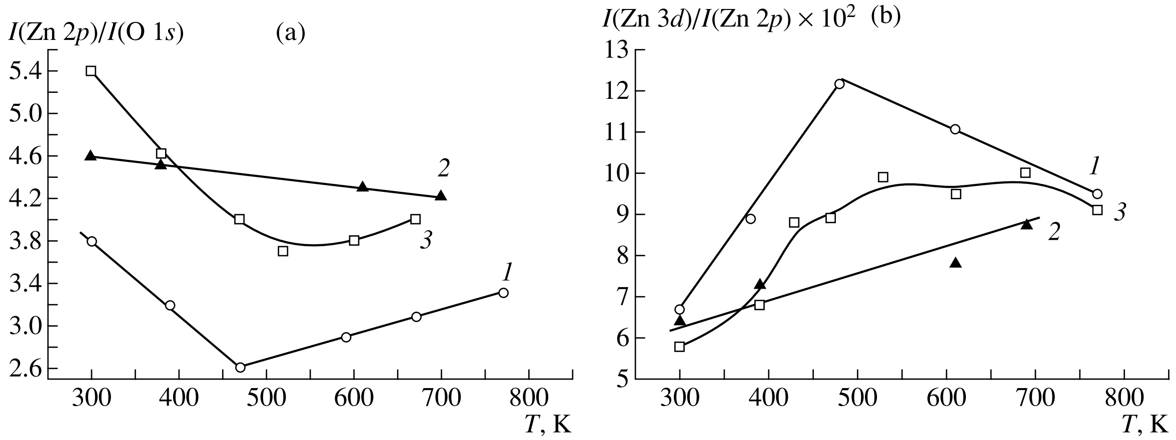

Fig. 7. Dependence of the peak intensity ratio for (a) Zn 2p and O 1s or (b) Zn 3d and Zn 2p on the temperature of treatment in oxygen for (*1*) parent ZnO and samples after mechanochemical activation for (*2*) 60 and (*3*) 600 s.

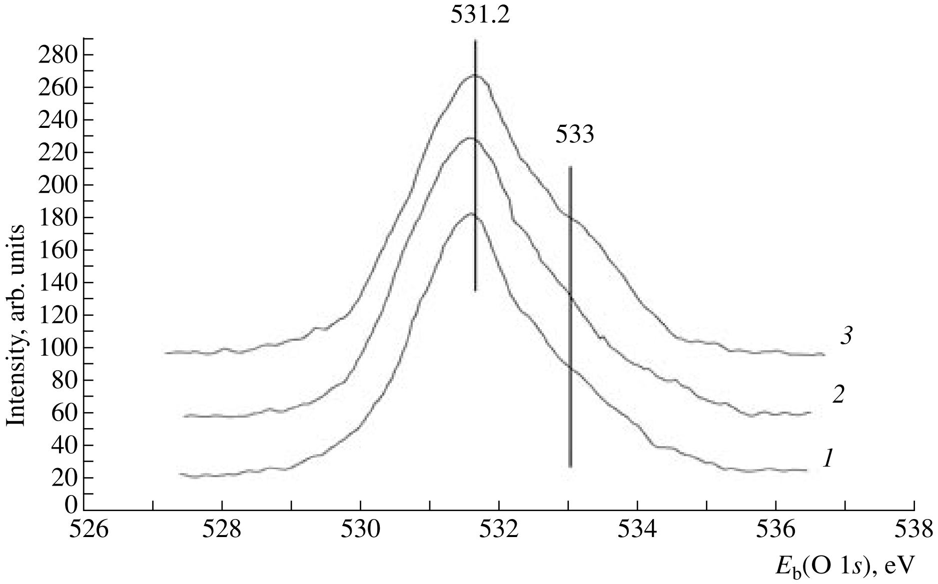

Fig. 8. The XPS spectra of O 1s for (*1*) the parent ZnO sample and ZnO samples activated for (*2*) 600 and (*3*) 60 s on heating to 700 K in an oxygen atmosphere.

whereas the adsorption of oxygen and the diffusion of zinc on the surface were observed at temperatures higher than 500 K. From Fig. 7, it follows that in the parent zinc oxide the diffusion of zinc from the bulk to the surface occurred at temperatures higher than 500 K; this diffusion in the sample activated for 600 s occurred at $T > 600$ K, whereas it was not observed in the sample activated for 60 s up to 700 K. The migration of zinc to the surface resulted in the disappearance of a peak at 533 eV from the O 1s spectra; that is, low-coordinated oxygen disappeared from the surface. In this case, the question arises: how is the bulk charge compensated? In our opinion, this takes place by the formation of conduction electrons and O^- radical anions, which are detected by EPR spectroscopy (see above).

Thus, mechanochemical activation resulted in an increase in the surface concentration of zinc; this stimulated the adsorption of oxygen on heating. This enhanced reactivity was due to the formation of both a fresh surface and defects after mechanochemical activation; oxygen, which was detected as a shoulder with E_b = 533 eV in XPS spectra, was sorbed at these defects. The thermal stability of sorbed oxygen depended on the time of mechanochemical activation, and the sample activated for 60 s exhibited a maximum thermal stability. This fact allowed us to suppose that the nature of oxygen was different in samples with different activation times. It is most likely that, in the sample with an activation time of 60 s, oxygen was sorbed at the outcrop sites of defects on the surface, whereas it

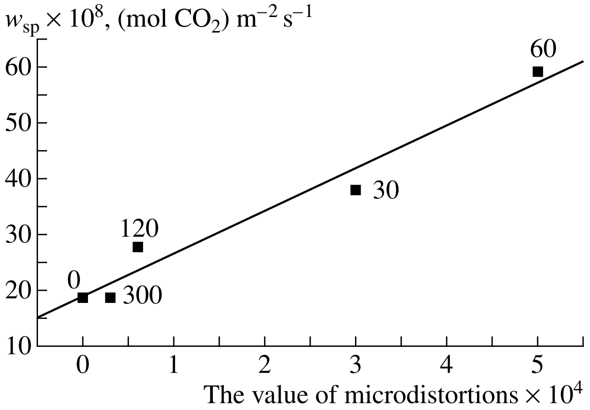

Fig. 9. Dependence of the specific rate of CO oxidation (w_{sp}) on the value of microdistortions (the figures specify the activation times in seconds).

was sorbed onto a freshly formed surface in the sample activated for 600 s. A comparison of these results with data on catalytic activity suggests that oxygen chemisorbed at the outcrop sites of defects on the surface took part in a catalytic reaction because among all of the samples studied by XPS the sample activated for 60 s exhibited enhanced catalytic activity.

CONCLUSIONS

In conclusion, we attempt to describe the nature of the effect of mechanochemical activation on the catalytic properties of zinc oxide. First, we repeat that mechanochemically induced point defects, which are superequilibrium defects, have no effect on the catalytic activity of ZnO in the reaction of CO oxidation under the test conditions. This is evidenced by the constancy of the catalytic activity of samples activated in a vibrating mill and in a disintegrator. These treatments resulted in the formation of a great number of point defects of differing natures, which disappeared on heating to the reaction temperatures of CO oxidation. At short activation times (30–60 s) in a planetary mill, extended defects (small-angle interblock boundaries) were formed in zinc oxide. Simultaneously, an increase in the specific catalytic activity was observed. An increase in the reactivity was also observed, which manifested itself in the appearance of oxidizing properties toward CO and hydrogen selenide in the sample, in the enhanced sorption of nickel salts from solutions, in a decrease in the reduction temperature of supported nickel chloride, and in an increase in the catalytic activity of compounds supported on the activated oxide, as described previously [15]. At activation times between 60 and 300 s, the intense fracturing of ZnO crystals with crystal structure relaxation was observed; in these samples, a decrease in the specific catalytic activity was observed, which reached a level typical of the parent sample at an activation time of 600 s, when a maximum degree of dispersion was reached. This behavior of the system suggests that the active centers of CO oxidation, which are responsible for an increase in activity, are centers located on the surface of crystallites at the outcrop sites of small-angle interblock boundaries, dislocations, and defects due to the displacement and turn of layers over distances shorter than those required for the formation of stacking faults. Oxygen chemisorbed at the outcrop sites of defects, which was detected by XPS, plays an important role in an increase in the specific catalytic activity. The Zn^+ ions, which are the constituents of defects, may serve as the sites of oxygen chemisorption. It is likely that this oxygen is an elementary active site. A linear correlation between the value of microdistortions due to the appearance of these defects and the specific catalytic activity serves as conclusive evidence of the implication of small-angle interblock boundaries, dislocations, and shear defects in the increase of catalytic activity (Fig. 9).

A small increase in catalytic activity at an activation time of 1800 s can be explained by the effect of stacking faults, which were observed in these samples. It is also probable that active centers were interblock boundaries in agglomerates formed at the specified activation times. The effect of stacking faults or interblock boundaries in agglomerates is much smaller than the effect of small-angle interblock boundaries. Another argument for the correctness of the above conclusions on the role of small-angle interblock boundaries in the increase of the catalytic activity is the fact that the disappearance of these defects either because of crystal structure relaxation as a result of the dispersion of crystals or as a result of thermal annealing decreased the catalytic activity to a level typical of the parent sample, as illustrated in Figs. 1 and 8.

It is likely that conduction electrons, which appear during defect formation, play an important role in the increase of the activity of zinc oxide. These electrons can participate in elementary acts related to electron transfer and facilitate the occurrence of these acts. In the parent ZnO, which is a semiconductor, the participation of catalyst electrons in these elementary acts is hindered.

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