Acid-base properties of the surface of zinc oxide powders subjected to milling in the attritor

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Abstract. Using the method of acid-base indicators adsorption, the influence of mechanical stresses and defects, arising in the milling process, on the surface properties of ZnO powders is analyzed. An explanation of the changes in acid-base properties is given.

1. Introduction

Due to its electrical, optical and structural properties, zinc oxide (ZnO) has been used as a catalyst, solar photocatalyst, phosphor, material for gas sensors, optoelectronic and piezoelectric devices, varistors, etc. [1–4]. Among methods of ultradisperse ZnO powders preparation for these applications, mechanical grinding in ball and planetary mills and attritors, is the most common [5, 6]. Currently, the physico-chemical processes occurring during the milling have been studied quite well. At the same time, knowledge of the change in the acid-base properties of the powder surface during grinding is very limited. It is well known that the acid-base properties of the surface correlate practically with all parameters of a solid (charge and radius of ions, the type of crystal lattice, the forbidden band, etc.), and also with surface reactivity, and hence with gas sensitive, catalytic, photocatalytic, luminescent, electrophysical, optical and other material properties [7, 8]. Therefore, it is important to know how the milling affects the acid-base properties of ZnO and whether it can be used as a controlled parameter in determining optimal treatment conditions for the development of ZnO-based materials for a specific applications?

The aim of this work is to study the changes in the acid-base properties of the surface of ZnO powders after grinding accompanied by the growth of defects and mechanical stresses in crystallites. As a tool of influence, the mechanical milling in the attritor (this “soft” grinding method allows to minimize the consequences of high-energy impacts appearing in planetary mills) is chosen.

2. Experimental

For the study, commercial ZnO powders (> 99.0%, Acros Organics, USA) were used. ZnO powders were subjected to mechanical grinding by a laboratory attritor (Batch-Lab HD / 01, UNION PROCESS, INC., USA); grinding bodies – ZrO₂ balls with a diameter of 3 mm; final ratio of the mass of milling bodies to the mass of zinc oxide was 18: 1; rotation speed 400 rpm. Milling was carried out in a medium
of isopropyl alcohol. Samples weighing 20 g were taken after 1, 3 and 5 hours of grinding. The selected samples were then dried for 24 hours at 70 °C.

The distribution of donor-acceptor centers on the surface of the resulting ZnO powders was studied by the method of the adsorption of acid-base indicators [9]. We used a set of indicators with pH values varying in the range from −4.4 to 14.2: ethylene glycol (pKa=14.2); indigocarmine (pKa=12.8); Nilián blue A (pKa=10.5); timol blue (pKa=8.8); bromothymol blue (pKa=7.3); bromocresol purple (pKa=6.4); methyl red (pKa=5.0); bromophenol blue (pKa=4.1); methyl orange (pKa=3.5); methanitroaniline (pKa=2.5); fuchsin (pKa=2.1); brilliant green (pKa=1.3); crystalline violet (pKa=0.8); o-nitroaniline (pKa=−0.3); 4-chloro-2-nitroaniline (pKa=−0.9); dinitroaniline (pKa=−4.4). The method for calculating concentration of active centers and Hammet acid function is given in [9].

Determination of the specific surface area of ZnO powders, S_{sp}, and the average particle size was carried out using the method of nitrogen thermal desorption and Sorbi MS device (Russia). X-ray diffraction spectra were measured using X-ray diffractometer DRO-3 (Russia). These data were used for calculation crystallite size and microstress, ε.

3. Results and discussion

Figure 1, a shows the distribution of adsorption centers on the surface of ZnO powders in the range pH = −4.4 ... 14.2 as well as data on specific surface area and acidity function Hammet. For convenience, data related to the centers with pH = −4.4 and 14.2 are presented with another scale. All submitted pH range can be divided into 4 areas [7]: pH<0 is the area of Lewis-type base centers; 0<pH<7 is the area of Brønsted-type acid centers; in the 7<pH<14 region, the Brønsted-type base centers are dominated; and in the pH>14 region the main centers are acid centers of the Lewis type.

Figure 1, b shows the commonly used model of active centers on the ZnO surface [8], which can be used to interpret the results obtained. According to this model, Lewis-type base centers with pH=−4.4 ... −0.3 are two-electron orbitals of surface oxygen atoms $\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\·
The concentration of such centers indirectly characterizes the concentration of vacancies in the zinc sublattice, VZn, on the surface of ZnO crystallites. The Brønsted-type base centers with pKa the range of 7.3 – 14.2 are represented by surface hydroxyl groups that have Zn-OH structure in various configurations. Apparently, their number correlates with the concentration of vacancies in the oxygen sublattice, VO. Acid centers of the Brønsted type with pKa= 0.8 ... 6.4 are protons bound to surface oxygen atoms in various configurations. Acid centers of the Lewis type with pKa= 14.2 are represented by surface zinc atoms experiencing a deficiency of neighbors, which may also be in various configurations.

Table 1 gives data characterizing the samples of powders studied: the specific surface area, S_sp; the average particle size, d_1; the size of the region of coherent scattering d_2 (crystallite size); microstress, ε; the total concentration of all centers, \( \sum Q(p\text{Ka}) \); and the Hammett acidity function, \( H_0 \).

| Parameters | Milling time, h |
|------------|----------------|
| S_{sp}, m^2/g | 0   | 1    | 3   | 5   |
| d_1, nm    | 5.4 | 6.1  | 7.6 | 10.0 |
| d_2, nm    | 197 | 176  | 141 | 107  |
| ε·10^3     | 3.1 | 3.5  | 3.9 | 5.8  |
| H_0        | 5.24 | 10.61 | 11.40 | 8.10 |
| \( \sum Q(p\text{Ka}) \), mmol/m^2 | 4.72 | 3.12 | 6.48 | 3.22 |

Using the X-ray phase analysis it was shown that the ZnO grain size (d_1) as well as the crystallite size (d_2) decrease almost linearly upon the increase of the milling time. At the same time the microtensions (ε) increased as a square function of the milling time. The grain size (d_1) is always larger than the crystallite size (d_2) (Table 1) so one can conclude that the grains are composed of a number of the crystallites.

The increase of the milling time to 3 hours results in a pronounced increase of the concentrations of the Lewis acid centers (pKa = 14.2) and of both the Bronsted base centers (pKa = 12.8) and the Bronsted acid centers (pKa = 2.5). Such phenomenon of the simultaneous appearance of an acid and a base adsorption centers spaced equally from the neutral point (pKa = 7) upon ZnO treatment was observed earlier in the ref. [9]. There was suggested that Zn and O bond breaking was responsible for the formation of the acid and base couple of centers related to the lattice oxygen and the lattice metal atom (figure 2). As a result, the overall concentration of the active centers is increased about 2.5 times upon 3 hours milling while the Hammet acidity function \( H_0 \) was not changed significantly between 1 hour and 3 hours of milling (table 1) as if the both the acid and the base centers appeared.

![Figure 2](image.png)

Figure 2. The schematics of the formation of the acid and of the base centers as a result of the Zn and O bond breaking.

The further increase of the milling time up to 5 hours results in the decrease of the overall concentration of the active centers and in the decrease of their energy measured as the overall deviation of their pKa from the 7 value (table 1). The concentration of the Lewis acid and base centers having pKa
= −4.4 и 14.2, respectively, was decreased while the concentration of the Lewis base centers (pKa = −0.3) and of the protons having pKa = 2.5 and 5 was increased. The appearance of the low base value centers having pKa = −0.3 is related to the appearance of the oxygen anions surrounded by the excess number of the Zn⁺ cations, which causes the reduction of the electron donating properties. The reduction of the electron donating properties of the surface oxygen anions is also caused by the increase of the concentration of the weak Brønsted acid centers with pKa = 5. As a result, after 5 hours of milling the Hₒ value was reduced to 8.1 and the overall concentration of the surface adsorption centers was decreased two times compared to the case of the powder subjected to 3 hours milling. The changes described above of the surface functionality of the ZnO powders studied after 5 hours of milling are in general indicative of the major surface restructuring including bond breaking induced by the milling treatment. It is worth to note that the changes of the concentrations of the various active sites on the ZnO surface were not at all monotonic upon the increase of the milling time.

4. Conclusion
It is shown that on the initial surface of ZnO powders, acid centers of the Lewis type with pKa = 14.2 and the base centers of the Lewis type with pKa = −4.4 dominate with approximately equal surface concentrations. The concentration of Brønsted-type centers is noticeably less. After milling, the surface basicity increases and the surface states spectrum transforms, affecting both Lewis and Brønsted-type centers. However, these changes do not follow any general pattern. It highlights the complexity of the processes occurring on the surface of ZnO crystallites in the milling process. A more detailed picture of the changes occurring on the ZnO surface was obtained as a result of studies based on a more detailed analysis of FTIR spectra and the use of additional analytical methods [10].

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