Effect of Mechanochemical Activation on the Catalytic Properties of Zinc Oxide

V. V. Molchanov, R. A. Buyanov, S. V. Tsybulya, G. N. Kryukova, A. N. Shmakov, A. I. Boronin, and A. M. Volodin

Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

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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 \( \text{H}_2\text{O}_2 \) 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 \( \text{H}_2\text{O}_2 \) 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 mecha-
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 mecha-nochemical activation in an EI $2 \times 150$ 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 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$_\alpha$ 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.

The surface of mechanically activated ZnO samples was studied by X-ray photoelectron spectroscopy (XPS). The studies were performed on a VG ESCALAB electron spectrometer. For the excitation of electrons, MgK$_\alpha$ 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 ($\tau = 30–60$ 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...