

Effect of Mechanochemical Activation on the Catalytic Properties of Ferrites with the Spinel Structure

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Abstract—It was found experimentally that stacking defects formed in the mechanochemical activation of zinc ferrite enhanced the specific catalytic activity in the reaction of CO oxidation. The specific rate of CO oxidation was a linear function of defect concentration, which was determined using Mössbauer spectroscopy and X-ray diffraction. A conclusion was drawn that the same centers are responsible for an increase in the catalytic activity, the sorption capacity for hydrogen sulfide, and the reactivity of zinc ferrite in the interaction with hydrochloric acid. It was assumed that analogous factors caused an increase in the catalytic activity and reactivity of magnesium ferrite.

INTRODUCTION

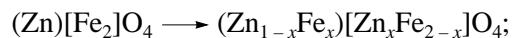
The determination of the nature of catalytically active centers is a fundamental theoretical problem of catalysis. The solution of this problem significantly affects the successful solution of the other problems of catalysis: the determination of catalytic reaction mechanisms, the development of a scientific basis for catalyst preparation, the elucidation of the nature of catalyst deactivation, etc.

The assumption that crystal structure defects are catalytically active centers has long been discussed in the literature. The supporters of this hypothesis presented many arguments, although all of them are indirect. In our opinion, the linear dependence of specific catalytic activity on the concentration of defects of a particular type can be strict and unambiguous evidence for the above statement. Methods for the correct determination of specific catalytic activity were developed and are used, however, the determination of the nature and concentration of crystal structure defects is a very complicated problem even for state-of-the-art physicochemical investigation 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 of defect on the catalytic activity. As a rule, researchers face this situation when studying defect systems prepared by traditional chemical methods.

To facilitate the solution of this problem, we used mechanochemical activation for the generation of defect structures. This technique allowed us to induce high concentrations of crystal structure defects and to generate mainly defects of one type. This provides an opportunity to identify defects and to determine their concentration.

As mentioned above, the determination of the nature of the defects is a very complicated problem. Therefore, in this study, we used systems that were thoroughly studied previously; first determining the reliability of relevant data published. Ferrites with spinel structure represent one of these systems studied in detail.

The effect of mechanochemical activation on the structure and physicochemical properties of ferrites with spinel structure has been studied in detail [1–4]. The majority of researchers were in agreement that the redistribution of cations between tetrahedral and octahedral sites of the spinel structure occurs during the mechanochemical activation of ferrites. This redistribution for normal and inverted spinels can be schematically represented as follows:



where sites with tetrahedral and octahedral coordinations are given in parentheses and square brackets respectively. Thus, in normal spinels, cations are redistributed between tetrahedra and octahedra, whereas in inverted spinels all the cations are transferred to sites with octahedral environments. Two opinions were expressed in the literature regarding the arrangement of cations with changed coordination in the crystal structure. One of them stated that cations are statistically distributed over the bulk of the substance, while the other said that the coordination environment is changed because of the displacement of oxygen layers in the crystallographic plane $\langle 111 \rangle$. Defects of this type are referred to as stacking defects. We believe that the latter opinion is more correct because the ordered arrangement of point defects (in this case, cations that changed coordination) is more energetically favorable than a sta-

tistical distribution. It is likely that cations that changed their coordination environment are concentrated at stacking defect sites. This is evidenced by the decomposition of zinc ferrite, activated for a long time, into oxides after heating to the temperatures of defect annealing [5]. At long activation times the concentration of stacking defects is high, and a great number of stacking defects are close to each other at certain locations. Evidently, if the rate of annealing of stacking defects is higher than the rate of diffusion of cations, zinc oxide and iron oxide phases are formed when a considerable portion of cations are concentrated at a particular location rather than statistically distributed over the bulk. Otherwise, it would be favorable for the system to relax into a spinel structure in the course of thermal treatment. We believe that the above structural changes, due to mechanochemical activation, affect the catalytic properties of ferrites with the spinel structure and stacking defects formed and enhance the specific catalytic activity.

EXPERIMENTAL

Magnesium ferrite and zinc ferrite as inverted and normal spinels, respectively, were used as the test materials. The samples were synthesized by the mechanochemical activation of corresponding oxide mixtures followed by calcination at 1170 K for 3 h. X-ray diffraction analysis revealed the presence of only magnesium ferrite and zinc ferrite phases in the samples without impurities of the parent oxides. Although the samples were prepared with the use of mechanochemical activation, the subsequent high-temperature treatment resulted in the complete annealing of defects, and the samples recovered to their original state.

The zinc ferrite and magnesium ferrite samples were subjected to mechanochemical activation in an AGO-2 centrifugal planetary mill in ceramic drums with corundum balls (the weights of the balls and the sample were 100 and 3 g, respectively; the drum speed was 13.3 s^{-1}). The specified conditions of activation allowed us to overcome a threshold effect, which is characteristic of spinel ferrites [2]. This effect is because in that defects are not formed at drum speeds lower than a certain value. To prevent the reduction of samples in the course of mechanochemical activation, an atmosphere of oxygen was produced in the drums with a pressure of 2–3 atm.

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

The specific catalytic activity of the samples was measured as the rate of CO oxidation per unit surface area of the samples. The reaction rate was determined under gradientless conditions in a flow-circulation reactor within the temperature range 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/O₂ molar ratio was 2).

The reaction products were analyzed by gas chromatography with the use of zeolite NaX as an adsorbent (for the determination of oxygen, nitrogen, and carbon monoxide) or *n*-butyric acid ester of triethylene glycol supported on IN3-600 (for the determination of CO₂). Before the analysis, carbon dioxide was separated from the other components of a mixture by freezing in a trap cooled with liquid nitrogen. A thermal-conductivity detector was used for the analysis.

The Mössbauer spectra were measured on a YaGRS-4 spectrometer. The sample and source temperatures were equal. Chemical shifts were determined with reference to α -Fe. The fraction of a mechanically activated state was determined at 78 K from the relative concentration of a magnetically ordered component, which corresponds to a sextet in the Mössbauer spectra. In turn, the relative concentration was determined by measuring the areas of spectral components.

RESULTS AND DISCUSSION

The study of the catalytic activity of zinc ferrite and magnesium ferrite mechanically activated for different times demonstrated that it underwent changes. Figure 1 shows the specific rate of CO oxidation as a function of the time of mechanochemical activation. It can be seen that this specific rate increased and flattened out at long activation times for both zinc ferrite and magnesium ferrite.

The time dependence of the catalytic activity (Fig. 1) is consistent with the buildup of the fraction of an activated state, as determined by Mössbauer spectroscopy [2] and X-ray diffraction analysis [6, 7] under the same activation conditions. The specific catalytic activity of magnesium ferrite increased more significantly than that of zinc ferrite. Thus, there is a qualitative correlation of the specific catalytic activity with the fraction of ferrites converted into an activated state. To obtain correct specific catalytic activities (primarily to remove the effect of the scatter of experimental points), the temperature dependence of the reaction rate was obtained at each time of activation. This dependence was described by linear functions in the $\log w$ – $(1/T)$ coordinates. The specific reaction rates of CO oxidation at 625 K were determined from these linear functions for samples with different times of mechanochemical activation. Next, the dependence of the specific rate of CO oxidation on the fraction of zinc ferrite transformed into an active state was plotted (Fig. 2). The fraction of the active state was determined from the relative intensity of a sextet in the Mössbauer spectra and taken from the published data [8]. It can be seen in Fig. 2 that an almost linear function is observed. This fact indicates that changes in the crystal structure of ferrites due to changes in the coordination of cations are responsible for an increase in the catalytic activity.

The dependence of the specific rate of CO oxidation on the degree of inversion of zinc ferrite, which was

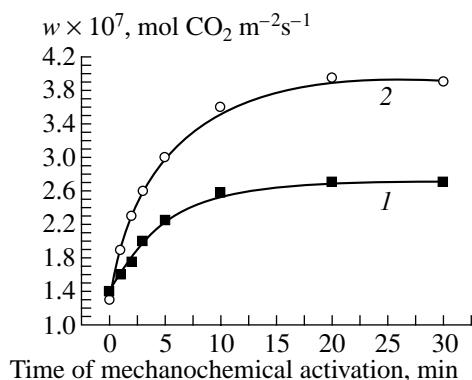


Fig. 1. Dependence of the specific rate of CO oxidation (w) on the time of mechanochemical activation for (1) zinc ferrite and (2) magnesium ferrite.

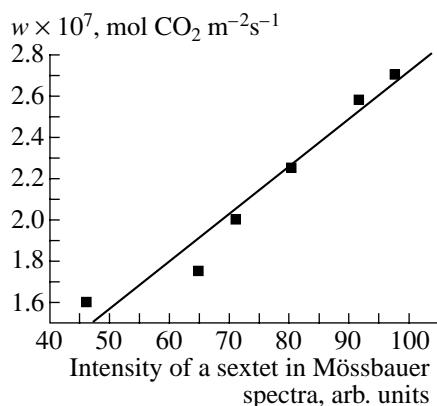


Fig. 2. Dependence of the specific rate of CO oxidation (w) on the amount of iron cations in a tetrahedral environment (according to Mössbauer spectroscopic data).

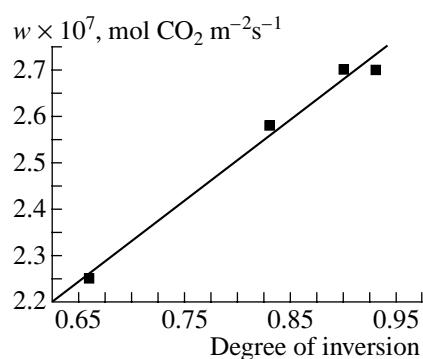


Fig. 3. Dependence of the specific rate of CO oxidation (w) on the degree of inversion of zinc ferrite [7].

determined from X-ray diffraction data [7], was plotted in a similar manner (Fig. 3). It can also be seen in Fig. 3 that an almost linear function is observed. Note that such a correlation of our data on the catalytic activity with published data is correct because the mechanical activation of samples was performed by Druska *et al.* [7] under conditions identical to those used in this work.

At temperatures higher than 650 K the active state disappeared and cations occupied their fixed places in the structure of spinels, as found using Mössbauer spectroscopy and X-ray diffraction analysis [2, 5]. The reaction at temperatures higher than 650 K resulted in a decrease in the specific catalytic activity of zinc ferrite or magnesium ferrite to a level of the initial unactivated samples. Figures 4 and 5 demonstrate that experimental points associated with activated samples at elevated temperatures fit the dependence for initial zinc ferrite and magnesium ferrite. The activity also decreased after the calcination of activated samples at temperatures higher than 650 K in air (Figs. 4, 5, points 3). The deactivation of samples on heating to high tempera-

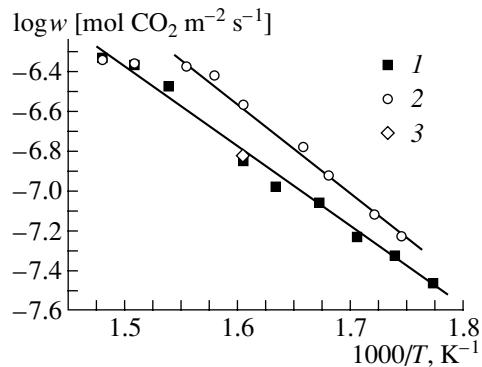


Fig. 4. The temperature dependence of the rate of CO oxidation for (1) initial and (2, 3) mechanically activated (20 min) zinc ferrite; in (3) the sample was calcined at 670 K.

tures, at which defects are annealed, additionally suggests that defects related to changes in the coordination environment of cations are responsible for the increase in the catalytic activity. In the course of catalyst testing, the specific catalytic activity decreased somewhat at temperatures no higher than 650 K; that is, a portion of the defects were annealed at temperatures lower than 650 K.

We attempt to describe the nature of active centers responsible for the increase in the catalytic activity of mechanically activated ferrite spinels using published data. An analysis of the crystal structure of a normal spinel suggests that the coordination of cations can be changed by disrupting the alternation of oxygen layers: in places ABAB packing occurred in place of ABCABC packing, which is characteristic of the structure of spinels [9]. An increase in the number of cations that changed their coordination corresponds to an increase in the number of stacking defects. In the case of an inverted spinel, a transition from the structure of spinel to the NaCl-type structure was observed. This transition also occurs via the formation of stacking defects with a

gradual increase in the number of fragments with ABAB-type packing. In this case, heterogeneous regions coherently joined to regions with the spinel structure were formed at an intermediate step. Finally, the ferrite is completely converted into a state with ABAB packing [2], which is characteristic of the NaCl-type structure.

An increase in the concentration of stacking defects resulted in an increase in the specific catalytic activity of zinc ferrite and magnesium ferrite. It is likely that the greater increase in the activity of magnesium ferrite was due to the formation of coherent heterogeneous regions with NaCl-type structure. Another difference between the behaviors of magnesium ferrite and zinc ferrite in the course of mechanochemical activation consists in changes in the activation energy. The activation energy of zinc ferrite was independent of the time of mechanochemical activation within the limits of experimental error and amounted to 75–80 kJ/mol. The activation energy of magnesium ferrite significantly decreased with the time of mechanochemical activation; in this case, the most considerable changes occurred at activation times longer than 3 min.

Activation energy of the reaction of CO oxidation on magnesium ferrite as a function of the time of mechanochemical activation

Time of mechanochemical activation, min	Activation energy, kJ/mol
0	70
1	69
2	63
3	52
5	42
10	41
20	41

This behavior of the system suggests that the decrease in the activation energy was due to the appearance of coherent heterogeneous regions. It is likely that the outcrops of stacking defects and coherent heterogeneous regions at the surface are different in the heats of chemisorption of the reactants; because of which, the activation energy decreases. For every activation time we have a certain set of sites with different energies of chemisorption at the surface; the averaged value of this energy is responsible for the apparent activation energy. Thus, we can state with confidence that the outcrops of stacking defects at the surface of crystallites are active sites responsible for an increase in the specific catalytic activity of zinc ferrite in the reaction of CO oxidation. This is almost unambiguously suggested by the above linear dependence of the specific catalytic activity on the concentration of stacking defects. In the case of magnesium ferrite, based on qualitative correlations, we believe that, in addition to stacking defects, active centers are also located on the surface of coherent heterogeneous regions. Note that these coherent heteroge-

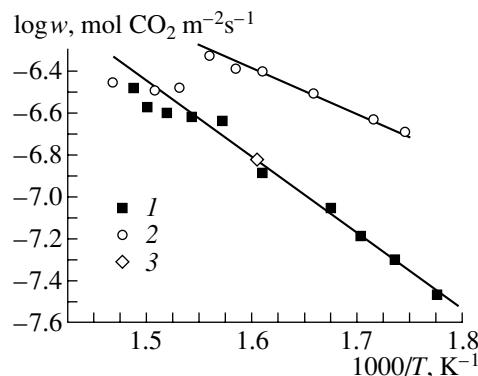


Fig. 5. The temperature dependence of the rate of CO oxidation for (1) initial and (2, 3) mechanically activated (20 min) magnesium ferrite; in (3) the sample was calcined at 670 K.

neous regions are stacking defect clusters. Therefore, the structures of active centers in zinc ferrite and magnesium ferrite are similar. However, differences in the catalytic properties suggest that, in the case of the formation of coherent heterogeneous regions, new qualities due to "collective" properties of stacking defects appear. The possible effect of other types of defects, which can be formed in the course of mechanochemical activation such as dislocations, should not be excluded. However, taking into account a very good approximation of the correlations to the linear dependence (Figs. 2, 3), the effect of other defects is very low or their concentration is not high.

It is most likely that the effect of stacking defects consists in changing the bond strength of oxygen at outcropped defects on the surface. It is well known that the oxidation of CO occurs by a stepwise mechanism, an elementary act of which is oxygen abstraction from the crystal lattice of a catalyst by a reactant molecule. In this case a maximum activity of the catalyst is reached at a certain optimum value of the bond strength of oxygen. Of course, additional studies are required to experimentally test this hypothesis.

The results obtained in this work together with published data allowed us to draw some general conclusions. Previously, we hypothesized that the same active centers (outcropped defects on the surface of crystallites) are responsible for an increase in the reactivity, sorption ability, and catalytic activity of solids [10, 11]. As demonstrated above, the outcrops of stacking defects on the surface of crystallites in zinc ferrite are responsible for the increase in the catalytic activity in the reaction of CO oxidation. According to published data [8], they are also responsible for an increase in the reactivity of ferrites toward hydrochloric acid and for an increase in the sorption capacity for hydrogen sulfide [5]. Thus, our previous hypothesis [10, 11] is supported by additional data. As for magnesium ferrite, the linear dependence of various kinds of chemical activity on the concentration of defects should be obtained in

order to draw analogous conclusions. Based on the indirect data available, we believe that a conclusion on the nature of active centers analogous to that made for zinc ferrite will be drawn.

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