Kinetics and Catalysis, Vol. 43, No. 1, 2002, pp. 122–128. Translated from Kinetika i Kataliz, Vol. 43, No. 1, 2002, pp. 132–139.
Original Russian Text Copyright © 2002 by Isupova, Tsybulya, Kryukova, Budneva, Paukshtis, Litvak, Ivanov, Kolomiichuk, Pavlyukhin, Sadykov.

Mechanochemical Synthesis and Catalytic Properties of the Calcium Ferrite $Ca_2Fe_2O_5$

L. A. Isupova*, S. V. Tsybulya*, G. N. Kryukova*, A. A. Budneva*, E. A. Paukshtis*, G. S. Litvak*, V. P. Ivanov*, V. N. Kolomiichuk*, Yu. T. Pavlyukhin, and V. A. Sadykov***

** Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
*** Institute of Solid-State Chemistry, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630128 Russia*

Received March 29, 2000

Abstract—The formation of the real structure of calcium ferrite prepared by the calcination of a mechanochemically activated hydroxide mixture at 600–1100°C was studied by X-ray diffraction analysis, electron microscopy, thermal analysis, Moessbauer spectroscopy, IR spectroscopy, small-angle X-ray scattering, and secondary-ion mass spectrometry. It was found that low-temperature calcium ferrite is an anion-modified oxide, in which the ordering of oxygen vacancies was incomplete. Regions with a disordered structure were detected on the surface of crystallites. As the calcination temperature was increased, the brownmillerite crystal structure was improved and the intercrystalline boundaries were formed and then annealed. At the surface, these processes were accompanied by a change in the predominant form of adsorbed NO from nitrosyl to dinitrosyl species. An increase in the specific catalytic activity of samples with calcination temperature can be associated with the perfection of the brownmillerite structure and with a change in the state of adsorption centers.

INTRODUCTION

Complex oxides with the perovskite structure are promising systems for the replacement of catalysts containing noble metals (Pt or Pd) in a number of high-temperature oxidation processes [1]. The coprecipitation and ceramic methods, which are commonly used for the synthesis of perovskites, exhibit a number of disadvantages. In the former method, a considerable amount of wastewater is produced. The latter method requires high temperatures (>1000°C) and long calcination times; consequently, the reaction product exhibits a low specific surface area. Mechanochemical activation considerably decreases the temperature and duration of the subsequent thermal treatment of reactants in the synthesis of perovskites as compared with the ceramic technology; thus, highly dispersed oxides can be prepared without a coprecipitation step [2]. The following factors are primarily responsible for the favorable effect of mechanochemical activation on the synthesis: dispersion and defect formation in starting reactants; the formation of a fresh surface, which accelerates chemical interaction between reactants; and the mixing of components on a molecular level [3–6]. In the last few years, the synthesis of complex oxide systems based on the acid–base interaction in the coactivation of hydroxides—mild mechanochemical synthesis—has been developed [7]. Calcium and iron hydroxides can be considered as such components of different basicity.

It was repeatedly noted that the use of various synthetic methods under nonequilibrium conditions (such as plasmochemical, mechanochemical, cryochemical, and explosion syntheses) makes it possible not only to prepare highly dispersed complex oxides but also to change their reactivity, for example, the specific catalytic activity in deep oxidation reactions [2, 8]. These effects can be associated with differences in the real (defect) structures of synthesized oxides and hence with changes in the state of active centers on the surface.

The structure of calcium ferrite (brownmillerite) is usually considered as anion-deficient perovskite with ordered oxygen vacancies, whose main structural motif consists of alternating octahedral and tetrahedral layers [9]. It is likely that the ordering of anion vacancies is not achieved by mechanochemical synthesis [10]. The subsequent thermal treatment results in the ordering of oxygen vacancies; this makes it possible to examine the effects of ordered and disordered anion vacancies on the catalytic activity and the state of adsorption centers.

The aim of this work was to study the genesis of the real structure of calcium ferrite prepared by a mechanochemical method with the subsequent thermal treatment and the effect of the real structure on the catalytic activity and the state of adsorption centers.

EXPERIMENTAL

Reagent-grade $Ca(OH)_2$ and α-FeOOH were used as starting compounds for the synthesis of $Ca_2Fe_2O_5$. The reagent mixtures were mechanically activated in an AGO-2 planetary mill (~10 W/g) in steel cylinders for 10 min. The weight ratio between the activated powder and grinding balls was 1 : 10. After activation, the samples were calcined at 400–1100°C.

0023-1584/02/4301-0122$27.00 © 2002 MAIK “Nauka / Interperiodica”

X-ray diffraction (XRD) analysis was performed on a URD-63 diffractometer using CuK_α radiation at a step of 1° in the range of 2θ angles 5°–80°.

Electron-microscopic data were obtained on JEM-100X microscopes (resolution, 0.5 nm).

Thermal analysis was performed on a DQ-1500 derivatograph in air or in a helium flow. The heating rate was 10 K/min.

The IR spectra of adsorbed NO in a region of 1000–4000 cm^{-1} were measured on a Bruker-113V spectrometer equipped with a diffuse-reflectance attachment. After evacuation at 500°C for 0.5–1 h, the samples were cooled to room temperature. The adsorption of NO on powders was performed at room temperature and a pressure of 10 torr. Absorption bands at 3000 cm^{-1} were due to an instrument effect.

Secondary-ion mass spectrometry (SIMS) was used for analyzing the surface and bulk composition of catalysts. The data were obtained on an MS-7201 instrument. The argon-beam energy was 4 keV, and the current density was 60 $\mu A/cm^2$. The dependence of the secondary ion current on the bombardment time was measured for samples supported on indium foil. Data on the surface composition were obtained after bombardment for 20 s to remove a monolayer and adsorbed gases from the surface. Data on the bulk composition of the samples were obtained after bombardment for 20 min, when the steady-state values of ion currents were attained. The relative error in the concentrations of elements was no higher than 20%.

The small-angle X-ray scattering (SAXS) data were obtained with the use of CuK_α radiation, a nickel filter, and an amplitude analyzer. The relative density of regions with changed electron density, primarily due to extended defects, was evaluated from the integral intensity of small-angle scattering [11].

The specific surface area was determined by the BET method.

The specific catalytic activity in the reaction of carbon monoxide oxidation in an excess of oxygen was determined in a batch-flow reactor at 400°C with the catalyst fraction of a particle size of 1–2 mm. The products were analyzed by chromatography. The flow rate of the reaction mixture (1 vol % CO in air) was 10 l/h; the circulation rate was 600–1000 l/h; the sample weight was 1 g. The error in the determination of reagent and product concentrations was no higher than 20%. The specific catalytic activity was calculated from the experimental degrees of CO conversion under the assumption that the reaction rate is a linear function of CO concentration.

RESULTS AND DISCUSSION

Based on XRD and thermal analysis data, Kosova *et al.* [10] drew the conclusion that the interaction between calcium hydroxide and iron hydroxide is absent at the stage of activation. The X-ray diffraction patterns of an activated hydroxide mixture exhibited only broadened reflections due to $Ca(OH)_2$, whereas thermal analysis revealed a decrease in the dehydration temperature of calcium hydroxide from 520°C in an initial sample to 440°C for a sample activated in the presence of goethite. These data are indicative of the activation of calcium hydroxide and on the formation of X-ray amorphous iron oxide in the course of the combined mechanical treatment of the hydroxides. However, additional studies of the activation products by Moessbauer spectroscopy suggest the occurrence of a mechanochemical reaction with the formation of an X-ray amorphous mixed oxyhydroxide.

Thus, the Moessbauer spectrum of an activated hydroxide mixture (Fig. 1) can be represented as the superposition of two singlets and a sextet. Based on the hyperfine splitting parameters of the sextet, this component with a relative intensity of ~10% can be attributed to α-Fe_2O_3. The intensity ratio between the singlets is equal to 1 to within the measurement error. Thus, it is believed that both singlets belong to the same doublet state of the iron ion, and the asymmetry of components results from the distribution of quadrupole splitting and isomer shift parameters, whose average values are equal to 0.62 and 0.35 mm/s, respectively (the isomer shift is given with respect to α-Fe). Based on the isomer shift, the doublet can be ascribed to the Fe^{4+} state in an octahedral oxygen environment [12].

The appearance of a paramagnetic doublet in the spectrum can be associated with the formation of small (~100 Å) superparamagnetic particles of iron oxide or hydroxide [13] in the course of mechanochemical activation, as well as with a chemical reaction in the hydroxide mixture. Because the activation of goethite results in the formation of α-Fe_2O_3, the spectrum of which is a symmetrical doublet with a quadrupole splitting of ~0.9 mm/s [14], the occurrence of a chemical reaction in the system cannot be excluded. Moreover, the mechanical treatment of crystalline $Ca_2Fe_2O_5$ in the presence and in the absence of water resulted in amorphization; in the former case, the Moessbauer spectra primarily exhibited a doublet [10].

According to XRD analysis (Fig. 2) and Moessbauer spectra (Fig. 1), the calcination of the resulting product in air at $T \geq 400$°C resulted in the formation of a crystalline brownmillerite phase of $Ca_2Fe_2O_5$ (JCPDS 19-222) and in the appearance of a Moessbauer spectrum typical of brownmillerite [15]. This low temperature of formation of a crystalline product from an activated hydroxide mixture suggests that an amorphous product is formed at the stage of activation. As the temperature of calcination was increased, lines in the diffraction pattern became narrower (Fig. 2). In this case, the specific surface area (BET) decreased and the X-ray particle size increased (Fig. 3a). The most pronounced change in the specific surface area took place on going from a calcination temperature of 600 to 700°C, whereas X-ray particle sizes determined for a peak at

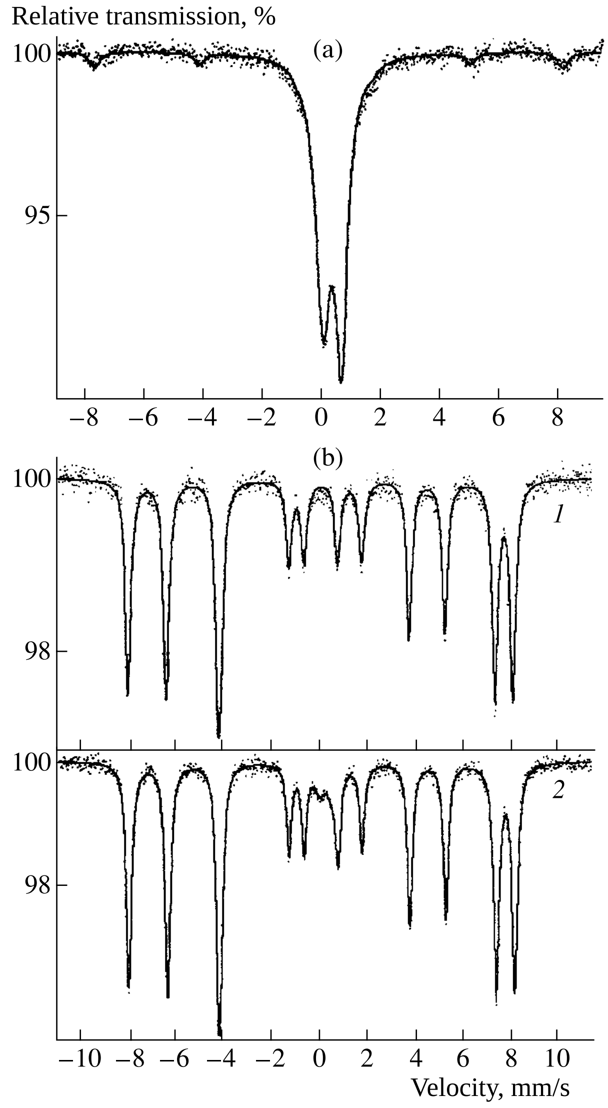

Fig. 1. Moessbauer spectra of a mixture of iron hydroxide and calcium hydroxide after (a) mechanical activation and (b) annealing at (*1*) 700 or (*2*) 900°C.

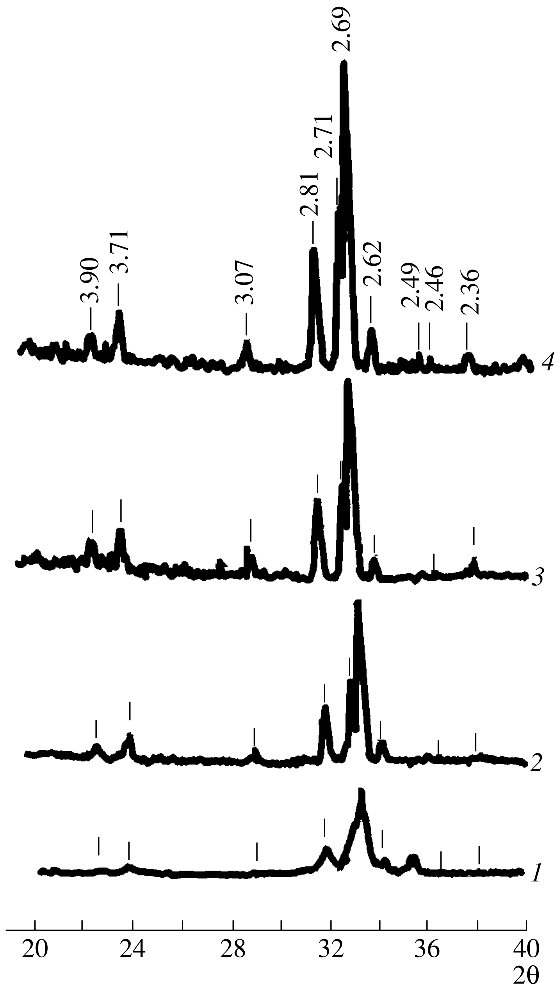

Fig. 2. Fragments of the X-ray diffraction patterns of calcium ferrite samples calcined at the following temperatures, °C: (*1*) 400, (*2*) 700, (*3*) 900, and (*4*) 1000.

$2\theta = 32°$ (reflection 200) did not change so dramatically. In high-temperature samples, the particle size was considerably smaller than the value determined derived from specific surface areas. Thus, we can draw the conclusion that the crystallites are microdomains, which was supported by electron microscopy.

Thermal analysis demonstrated (these data are not given here for brevity) that no thermal effects were detected in the DTA curves of samples calcined at 800 and 1000°C. It is likely that lower temperature samples are anion-modified because a decrease in weight was observed on heating them. For example, the weight of a sample calcined at 600°C decreased by ~8–10% in the following three temperature regions: 100–150°C (3%), 200–500°C (2%), and 620°C (3.5%). Although it is difficult to distinguish well-defined thermal effects, a diffuse endothermic effect at 100–650°C can be attributed to the presence of hydroxyls and carbonate ions, which are removed as water and CO_2 on heating, in the sample. The presence of these anions can also result from an impurity fraction of parent hydroxides and carbonates (<5%).

Thus, the results suggest that a crystalline brownmillerite phase was not formed at the stage of activation of a hydroxide mixture, probably because of a positive thermodynamic potential ($\Delta G°$) of the reaction [10]; however, the possibility of the formation of a combined amorphous hydrated product cannot be ruled out. It is likely that an anion-modified brownmillerite phase was formed after thermal treatment at 400°C (based on the data of XRD and thermal analysis and Moessbauer spectroscopy). It is of interest that the storage of an activation product also resulted in the formation of crystalline brownmillerite with an X-ray particle size of ~150 Å. A further increase in the calcination temperature resulted in an increase in the crystallite size and in an improvement in the brownmillerite structure.

According to electron-microscopic data, the following two types of particles can be recognized in the activation product: coarse (~1 μm) crystallites, which are characterized by single-crystal microdiffraction, and aggregates (~1 μm) of crystallites (~150–200 Å). Very small particles (~40 Å) also occurred, which can be most likely assigned to an α-Fe_2O_3 impurity. After calcination at 600°C, aggregates with a size of ~1 μm were retained; the crystallite size in an aggregate increased up to ~250 Å. This sample is characterized by a ring (powder) microdiffraction pattern (Fig. 4). The surface of crystallites exhibits regions with disordered structures: rough split edges and very small (~4 nm) crystallites. The size of crystallites that constitute an aggregate increased with calcination temperature. In this case, disordered regions occurred on the surface up to a temperature of 900°C. It is likely that mosaic crystals of size ~1 μm with a microdomain size of ~500 Å were formed in a sample calcined at 900°C as a result of sintering of individual crystallites. Some extended reflections in the SED pattern agree with the microdomain structure of particles. A further increase in the calcination temperature resulted in the annealing of grain boundaries and in the formation of single crystals. A sample calcined at 1000°C exhibited mixed-type microdiffraction, which combined single-crystal and microdomain types, whereas only single-crystal microdiffraction was observed after calcination at 1100°C. Thus, the microstructure of particles changed simultaneously with an increase in the crystallite size. Crystallites in an aggregate were randomly oriented (ring microdiffraction pattern) in a sample calcined at 600°C, whereas a further increase in the calcination temperature initially resulted in the formation of intercrystalline boundaries (with microdiffraction typical of particles with the microdomain structure) and then, in the annealing after calcination at 1100°C (single-crystal microdiffraction).

The dependence of the relative concentration of regions with nonuniform electron density in the samples on calcination temperature was studied by SAXS. Note that in all samples several types of such regions were detected, which were different in characteristic sizes. In samples calcined at 600–900°C, the sizes of regions were 60, 120, 180, and 220 Å, which can correspond to different sizes of microinclusions of the same composition in the matrix of a different composition. As the calcination temperature was increased from 600 to 1000°C, initially only the integral intensity of scattering from these regions decreased (up to 900°C); this fact indicates that the samples became more homogeneous. A further increase in the calcination temperature up to 1000°C resulted in an increase in the size of inhomogeneity regions and in the appearance of a new main scattering region of size ~30 Å. A region of the above size can appear because of the formation of coherent grain boundaries (electron microscopy) or twin boundaries in brownmillerite crystals [16].

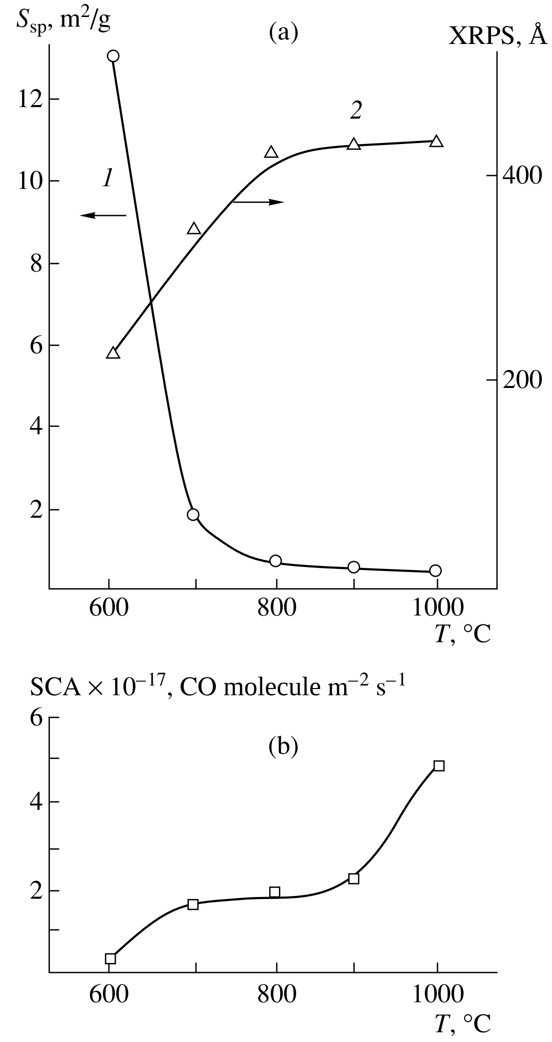

Fig. 3. (a) (*1*) Specific surface area, (*2*) X-ray particle size (XRPS), and (b) specific catalytic activity (SCA) as functions of the temperature of calcination of calcium ferrite samples.

The studies of samples performed by SIMS and IR spectroscopy allowed us to conclude that the low-temperature samples of calcium ferrite can be anion-modified, and this circumstance can also be responsible for their specific catalytic activity.

A change in the elemental composition was analyzed by measuring the following ratios between ion currents: $^{54}Fe/^{40}Ca$ and $^{16}O/^{40}Ca$ ($^{112}Ca_2O_2/^{56}CaO$). An observed increase in the molecular ion emission of $^{80}Ca_2/^{40}Ca$, $^{96}Ca_2O/^{40}Ca$, and $^{112}Fe_2/^{56}Fe$ and a decrease in the emission of $^{44}CaOH$ and oxygen with increasing temperature of calcination reflect the improvement of the structure of a brownmillerite phase on calcination. In this case, the ratio between ion currents, $^{54}Fe/^{40}Ca$, remained almost unchanged. This fact is indicative of the absence of the segregation of one or another cation on the surface of samples.

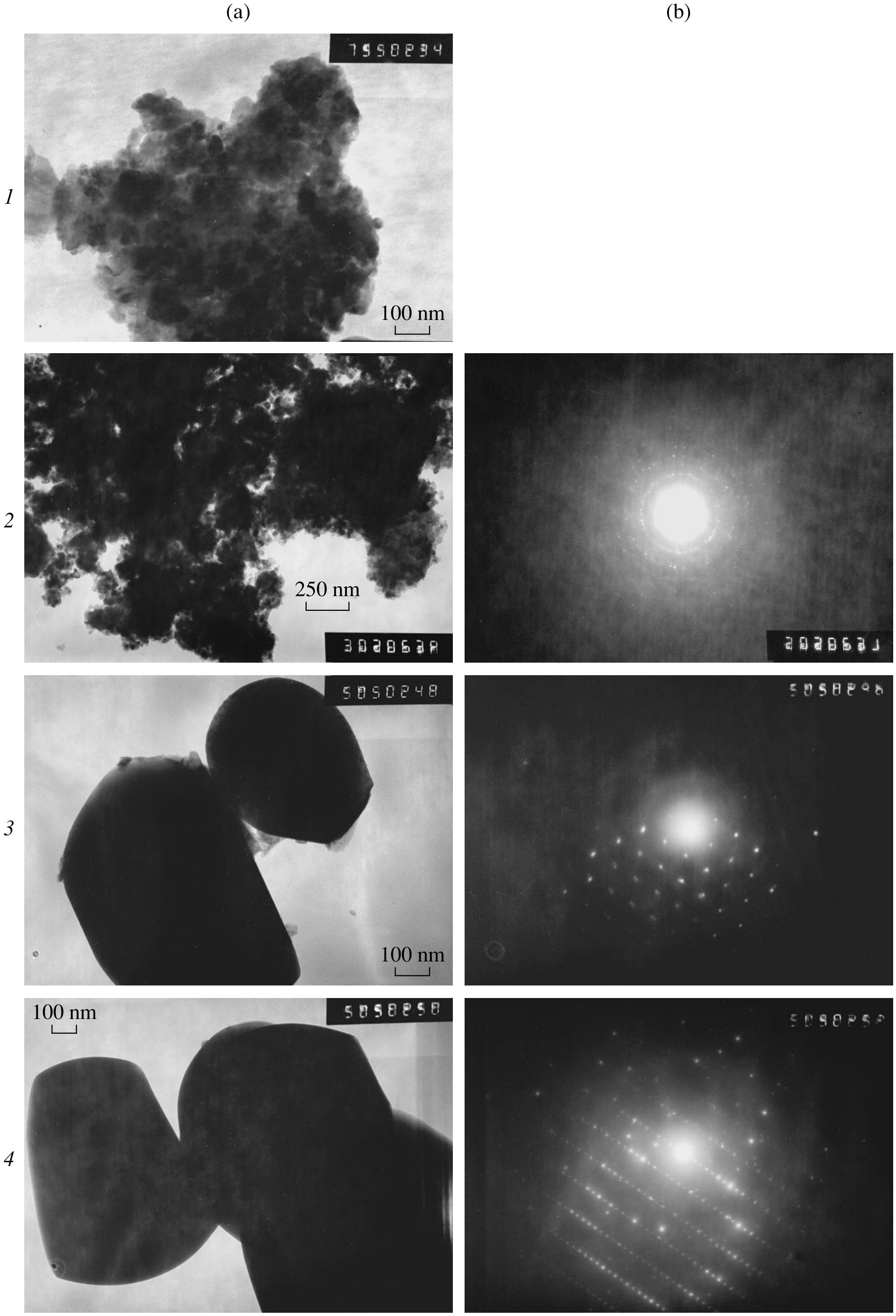

Fig. 4. (a) Electron micrographs and (b) microdiffraction patterns of calcium ferrite samples calcined at different temperatures: (*1*) without thermal treatment, (*2*) 600°C, (*3*) 900°C, and (*4*) 1100°C.

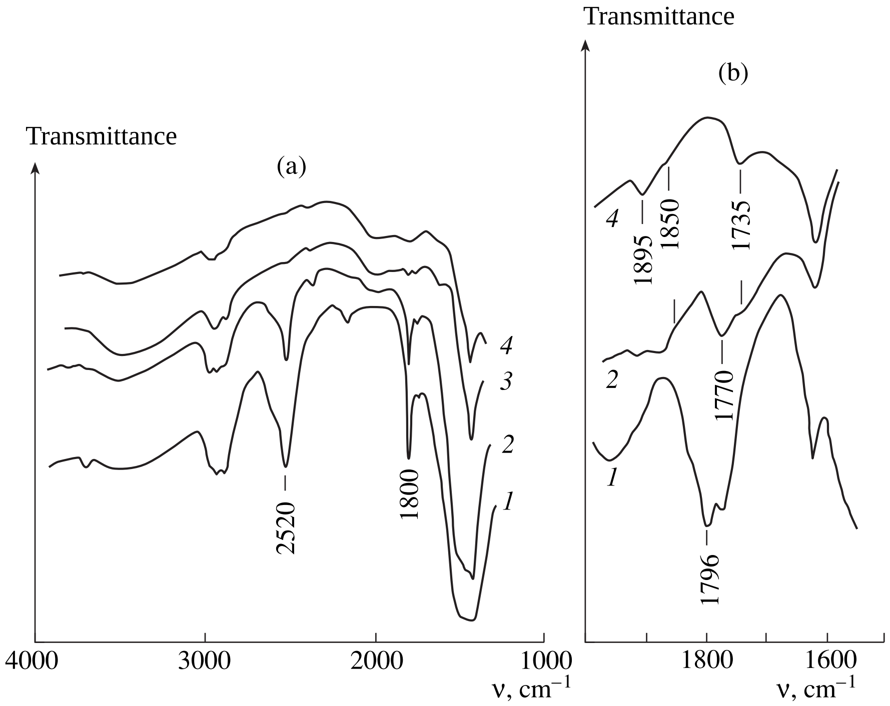

Fig. 5. IR spectra of (a) calcium ferrite samples and (b) NO adsorbed on calcium ferrite samples depending on calcination temperatures, °C: (*1*) 600, (*2*) 700, (*3*) 1000, and (*4*) 1100.

According to IR-spectroscopic data (Fig. 5), an intense absorption at 1400–1500 cm^{-1} is observed in the samples calcined at 600–900°C. This absorption is typical of carbonate structures of the monodentate type [17]. The spectra of samples after calcination at 1000–1100°C exhibited only a weak band at 1430 cm^{-1} in this region; this band is characteristic of the symmetrical carbonate ion. These absorption bands can be primarily due to the surface anion modification of the synthesized oxide because the spectra were measured in the diffuse-reflectance mode. Moreover, it is likely that calcium carbonate was present in the samples; this follows from the presence of characteristic absorption bands at 2520 and 1800 cm^{-1} in the spectra of powders; the intensities of these bands also decreased as the calcination temperature was increased [17].

We examined the catalytic activity of samples prepared at different temperatures and found that the specific catalytic activity was not constant and increased with calcination temperature (Fig. 3b). This change was not associated with a change in the relative concentration of surface iron cations. An increase in the specific catalytic activity of samples occurred in parallel with the improvement of the crystal structure of a calcium ferrite surface because of the removal of residual carbonate and hydroxyl groups and the formation of coherent grain boundaries. These surface processes may be accompanied by changes in the state of active centers (their amount and quality).

Indeed, we found by IR spectroscopy of adsorbed NO test molecules (Fig. 5) that the state of adsorption centers was changed with calcination temperature. In the spectra of NO adsorbed on calcium ferrite calcined at 600°C, fundamental absorption bands at 1770–1800 cm^{-1} due to NO complexes with clustered Fe^{+2} + ions [18], as well as an absorption band at 1950 cm^{-1} and a narrow absorption band at 1610 cm^{-1}, can be recognized. An increase in the calcination temperature up to 700°C caused a decrease in the intensity of the absorption bands at 1770–1800 cm^{-1} and the appearance of absorption bands at 1895 and 1735 cm^{-1}, whereas the absorption band at 1610 cm^{-1} remained almost unchanged. After calcination at 1100°C, the absorption bands at 1770–1800 cm^{-1} disappeared, and the absorption bands at 1895 (with a shoulder at 1850 cm^{-1}), 1735, and 1610 cm^{-1} were retained. By analogy with the spectrum of NO adsorbed on lanthanum ferrite [19], it is likely that the absorption bands at 1790–1800 cm^{-1} in low-temperature samples can be ascribed to NO adsorbed on Fe^{2+} clusters formed on the surface of perovskite. The formation of dinitrosyl complexes with coordinatively unsaturated Fe$^{(2-\delta)+}$ cations also cannot be excluded in the case of low-temperature samples, as evidenced by the occurrence of weak absorption at 1850 and 1735 cm^{-1}. An absorption band at 1610 cm^{-1} can be attributed to nitrite–nitrate complexes bound to regular Fe$^{(3-\delta)+}$ centers, and absorption bands at 1950 and 1895 cm^{-1}, to the vibrations of NO adsorbed on these centers. A decrease in the vibration frequency of the N–O bond with calcination temperature can be indicative of a decrease in the coordination environment of these centers (for example, the appearance of tetrahedral $Fe^{(3-\delta)+}$ cations). The above data provide support for a change in the state of adsorption centers in calcium ferrite with calcination temperature. This change is symbatic with the removal of anions and, probably, the ordering of vacancies. It is well known that the adsorption of NO on regular octahedral $Fe^{(3-\delta)+}$ centers occurs with the formation of adsorbed NO and nitrite–nitrate species. Because the vibration frequency of adsorbed NO, which is sensitive to changes in the cation coordination, changed with calcination temperature, this may be indicative of differences in the coordination of $Fe^{(3-\delta)+}$ centers. Only low-temperature samples exhibited clustered, coordinatively unsaturated Fe^{2+} centers, which adsorb NO (these centers are typical of a defect perovskite structure). The molecules of NO were adsorbed as dinitrosyl complexes on low-coordination $Fe^{(2-\delta)+}$ centers. Thus, upon calcination, clustered Fe^{2+} centers, which are typical of a defect perovskite structure and adsorb NO, disappeared; octahedral $Fe^{(3-\delta)+}$ centers (1), which adsorb nitrite–nitrates, remained unaffected; the coordination of octahedral $Fe^{(3-\delta)+}$ centers (2), which form mononitrosyl complexes, decreased (probably down to tetrahedral); and the amount of low-coordination $Fe^{(2-\delta)+}$ centers (3), which form dinitrosyl complexes, changed. In this case, an increase in the specific catalytic activity with calcination temperature can result from the appearance of low-coordination centers (2) and (3) on the surface of calcium ferrite. These centers appear because of both the removal of surface anions and the formation of additional lowest coordination centers capable of forming dinitrosyls at the outlet of grain boundaries on the surface [20].

CONCLUSION

Thus, we examined the dependence of the real structure of mechanochemically synthesized calcium ferrite on the temperature of calcination. We found that low-temperature samples are anion-modified and the ordering of oxygen vacancies in these samples remained incomplete. Clustered Fe^{2+} centers, which are typical of a defect perovskite structure, are predominant adsorption centers on the surface of these samples.

An improvement in the crystal structure of brownmillerite due to the removal of anions and the ordering of oxygen vacancies, which took place as the calcination temperature was increased, was simultaneously accompanied by sintering processes: the size of crystalline grains increased and grain boundaries were formed and then annealed. In this case, surface adsorption centers changed because of the appearance of low-coordination tetrahedral iron cations, which appear in going from nitrosyl to dinitrosyl as the predominant species of adsorbed NO.

As the calcination temperature was increased, the specific catalytic activity of samples changed symbatically with the improvement of the crystal structure of brownmillerite and with the appearance of centers with a tetrahedral coordination of iron cations on the surface.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 99-03-32836).

REFERENCES

1. Tejuca, L.G., Fierro, J.L.G., and Tascon, J.M.D., *Adv. Catal.*, 1989, vol. 36, p. 237.
2. Isupova, L.A., Sadykov, V.A., Solov'eva, L.P., *et al.*, *Preparation of Catalysts: VI. Scientific Bases for the Preparation of Heterogeneous Catalysts*, Amsterdam: Elsevier, 1995, p. 637.
3. Zolotovskii, B.P., Klevtsov, D.P., Paramzin, S.M., and Buyanov, R.A., *Mekhanokhimicheskii sintez v neorganicheskoi khimii* (Mechanochemical Synthesis in Inorganic Chemistry), Novosibirsk: Nauka, 1991, p. 125.
4. Boldyrev, V.V., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, p. 2228.
5. Avvakumov, E.G., *Mekhanicheskie metody aktivatsii khimicheskikh protsessov* (Mechanical Methods of Activating Chemical Processes), Novosibirsk: Nauka, 1986.
6. Zyryanov, V.V., *Neorg. Mater.*, 1999, vol. 35, no. 1, p. 1.
7. Avvakumov, E.G., *Khim. Inter. Ust. Razv.*, 1994, vol. 2, nos. 2–3, p. 541.
8. Sadykov, V.A., Isupova, L.A., Tikhov, S.F., and Kimkhai, O.N., *Synthesis and Properties of Advanced Ceramic Materials*, 1995, vol. 386, p. 293.
9. Rao, C.N.R., Gopalakrishnan, J., and Vidyasagar, K., *Indian J. Chem.*, 1984, vol. 23A, p. 265.
10. Kosova, N.V., Devyatkina, E.T., Avvakumov, E.G., *et al.*, *Neorg. Mater.*, 1998, vol. 34, no. 4, p. 478.
11. Sadykov, V.A., Tikhov, S.F., and Kryukova, G.N., *J. Solid State Chem.*, 1988, vol. 74, p. 200.
12. Menil, F., *J. Phys. Chem. Solids*, 1985, vol. 46, no. 7, p. 763.
13. Pavlyukhin, Yu.T., *Doctoral (Chem.) Dissertation*, Novosibirsk: Inst. Solid State Chem., 2000.
14. Pavlyukhin, Yu.T., Medikov, Ya.Ya., Avvakumov, E.G., *et al.*, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim.*, 1979, no. 4, p. 14.
15. Benlovcif, R., Nguen, N., Greneche, J.N., and Raveau, B., *J. Phys. Chem. Solids*, 1990, vol. 51, no. 1, p. 79.
16. Rao, C.N.R. and Gopalakrishnan, J., *New Directions in Solid State Chemistry: Structure, Synthesis, Properties, Reactivity, and Materials Design*, Cambridge: Cambridge University Press, 1986.
17. Davydov, A.A., *IK-spektroskopiya v khimii poverkhnosti oksidov* (IR Spectroscopy Applied to the Chemistry of Oxide Surfaces), Novosibirsk: Nauka, 1984.
18. Tikhov, S.F., Sadykov, V.A., Kryukova, G.N., and Razdobarov, V.A., *Mendeleev Commun.*, 1994, p. 69.
19. Isupova, L.A., Budneva, A.A., Paukshtis, E.A., and Sadykov, V.A., *J. Mol. Catal.*, 2000, vol. 158, no. 1, p. 275.
20. Sadykov, V.A., Tikhov, S.F., Tsybulya, S.V., *et al.*, *Stud. Surf. Sci. Catal.*, 1997, p. 1155.