*Kinetics and Catalysis, Vol. 41, No. 2, 2000, pp. 287–291. Translated from Kinetika i Kataliz, Vol. 41, No. 2, 2000, pp. 315–320.*
*Original Russian Text Copyright © 2000 by Isupova, Yakovleva, Tsybulya, Kryukova, Boldyreva, Vlasov, Alikina, Ivanov, Sadykov.*

# Physicochemical and Catalytic Properties of $La_{1-x}Ca_x FeO_{3-0.5x}$ Perovskites

**L. A. Isupova*, I. S. Yakovleva**, S. V. Tsybulya*, G. N. Kryukova*, N. N. Boldyreva*, A. A. Vlasov*, G. M. Alikina*, V. P. Ivanov*, and V. A. Sadykov***

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

Received August 17, 1998

**Abstract**—The phase analysis of $La_{1-x}Ca_xFeO_{3-0.5x}$ perovskites prepared by a ceramic process from oxides is studied by X-ray diffraction and differential dissolution methods. At $x < 0.5$, the system does not form a continuous series of homogeneous solid solutions and does not consist of the members of a homological series. At $x < 0.5$, the system contains two phases and calcium ferrite nanoparticles located on the surface of lanthanum ferrite. At $x > 0.5$, the formation of the structures of a brownmillerite-based homological series is found. The catalytic activity of perovskites depends nonmonotonically on the $x$ value and reaches the maximum at $x = 0.6$.

## INTRODUCTION

The defect structure of perovskites (oxides with the overall formula $A^1_{1-x}A^2_x BO_{3-y}$ is one of the factors that affect their catalytic activity in various reactions of complete oxidation. It is commonly accepted that the substitution of lanthanum for an alkaline-earth cation results in either the appearance of vacancies in the oxygen sublattice or an increase in the charge on the cations of a sublattice B. Both effects can take place simultaneously [1]. The substitution of lanthanum for calcium in $La_{1-x}Ca_xFeO_{3-y}$ perovskites should cause the appearance of vacancies in the oxygen sublattice, because the $Fe^{4+}$ cation is unstable. According to Wu *et al.* [2], weakly bound oxygen adsorbs on the vacancies, and the catalytic activity of perovskite is proportional to the amount of this oxygen.

On the other hand, the model of structural ordering of the oxygen vacancies that has been proposed in [3–6] assumes the formation in this series of perovskites of a homological series of the overall formula $A_nB_nO_{3n-1}$ (A = La, Ca; B = Fe), where $n = 2, 3, 4 \ldots \infty$. The members of the series differ in the sequences of octahedral and tetrahedral layers. In these terms, perovskite $LaFeO_3$ is a member of the homological series with $n = \infty$ (only octahedral layers are present, OOOO…), and brownmillerite $Ca_2Fe_2O_5$ is a member of the series with $n = 2$ (with altering octahedral and tetrahedral layers, OTOTOT …). The member of the homological series with $n = 3$ (OOTOOT …), $La_{0.33}Ca_{0.67}FeO_{2.67}$, has also been found and described. The authors of [5] believe that the point defects are randomly distributed over the system at $x \le 0.5$ and the anionic vacancies are ordered at $x > 0.5$. At $x = 0.5$ ($La_{0.5}Ca_{0.5}FeO_{2.75}$), the system is in the transition between order and disorder.

According to the literature data, this system can exist in both the point-defect (probably for $x < 0.5$) and structurally ordered states ($x > 0.5$). In addition, structural ordering can be accompanied by the formation of a microdomain structure under certain conditions [6]. The presence of this structure enhances the catalytic activity [7–9]. The goal of this work was to study the catalytic activity of this series of perovskites depending on the real structure of oxides.

## EXPERIMENTAL

*Catalysts.* Samples of the $La_{1-x}Ca_xFeO_{3-0.5x}$ composition ($x$ = 0, 0.2, 0.4, 0.6, 0.8, and 1) were prepared by the ceramic process at 1100°C for 11–150 h with repeated intermediate grinding. The $La_2O_3$ obtained by the calcination of $La(NO_3)_2$ (chemical purity grade) at 500°C for 4–5 h, as well as $Fe_2O_3$ and CaO (both chemically pure), were used as starting reagents.

*The methods of study.* The samples were investigated by X-ray phase analysis, differential dissolution, high-resolution electron microscopy, and secondary ion mass spectrometry.

X-ray phase analysis (XRD) was carried out on an URD-6 diffractometer with $CuK_\alpha$ radiation. X-ray diffraction patterns were recorded on a tape with a velocity of 1 deg/min in the range of angles $2\theta = 10°–70°$. To estimate the phase composition in more detail (to reveal phases in small amounts and weak superstructural reflexes), the X-ray diffraction patterns were recorded at a step of $2\theta = 0.02°$ and time of accumulation of 30 s in each point.

The method of differential phase dissolution is based on separating the solubility regions for various phases with varied temperature and acidity [10]. The temperature of a solution was increased from 20 to

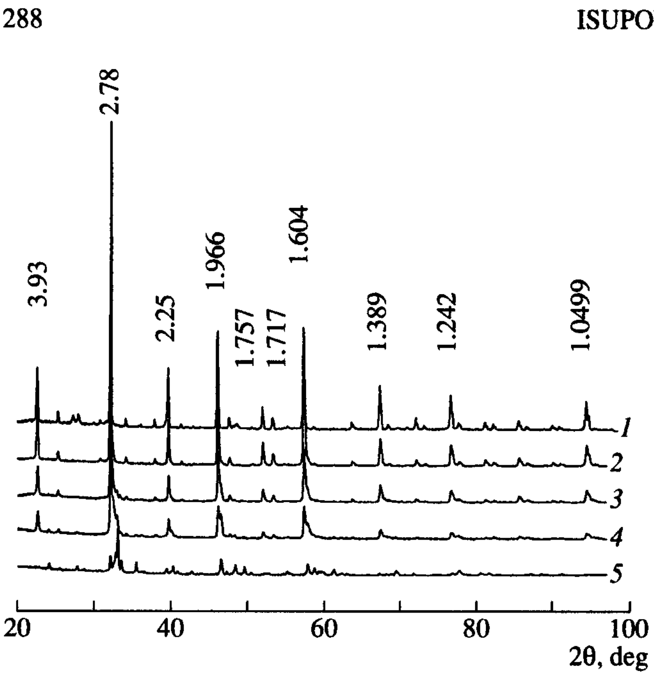

**Fig. 1.** X-ray diffraction patterns obtained by scanning for the samples of the $La_{1-x}Ca_xFeO_{3-0.5x}$ series: (*1*) $LaFeO_3$; (2) $La_{0.8}Ca_{0.2}FeO_{2.9}$, (*3*) $La_{0.6}Ca_{0.4}FeO_{2.8}$, (*4*) $La_{0.4}Ca_{0.6}FeO_{2.7}$, and (*5*), $La_{0.2}Ca_{0.8}FeO_{2.6}$.

90°C. HCl solutions with concentrations ranging from 1 to 10 N were used to dissolve the samples. The components of a solution were analyzed by atomic emission spectroscopy with an inductively bound plasma. Photometry was conducted on a BAIRD instrument (Netherlands).

The electron-microscopic patterns were obtained on a JEM-2010 microscope with a resolution of 3 Å.

The specific surface area was determined by the BET method from the data on the argon thermal desorption at 300°C.

Analysis by the secondary ion mass spectrometry (SIMS) was carried out on a MS-7201 instrument. The surface and bulk compositions of the samples were estimated. The energy of argon ions was 4 keV, and the current density of a beam was 60 $\mu A/cm^2$. To prevent charging of the samples during bombardment, they were supported on indium foil. The secondary ion currents of $La^+$, $Ca^+$, and $Fe^+$ as functions of the exposure were determined. The data concerning the surface were measured after treating the samples in the chamber for the 66 s sufficient to remove the adsorbed gases. To obtain the data on the bulk, the treatment was carried out for 1000 s until the steady-state values of the ionic currents were achieved. At the etching rate of 5 Å/min, the time lengths correspond to the thickness of the sputtered layer of nearly 5 and 100 Å, respectively. The relative error of experiment was less than 20%.

The catalytic activity of samples was determined in the model reaction of CO oxidation at temperatures of 400, 450, and 500°C in a flow-circulating reactor over the fractions of catalysts with the particles 0.5–1 and 1–2 mm in sizes. The weighed catalyst loading was 1 g, the circulation rate was 1200 l/h, and the feed rate of the reaction mixture (1% CO + 1% $O_2$ in He) was 10 l/h. The reaction mixture was analyzed by GC.

## RESULTS AND DISCUSSION

*Phase composition.* The phase composition of samples as a function of calcination time showed that a significant amount of the perovskite phase forms already after calcination for 11 h. The fraction of this phase increased with time of calcination, and its structure became more ordered. Table 1 presents the phase composition of the samples prepared by calcination for 150 h, which was determined by XRD and differential dissolution. Figure 1 shows the fragments of X-ray diffraction patterns. Phase analyses will be discussed in detail below. The chemical formulas of the samples correspond to the chosen stoichiometry of cations and the requirement of electroneutrality.

*$LaFeO_3$.* This sample is usual orthorhombic perovskite with the following unit cell parameters: $a = 5.567$ Å, $b = 7.855$ Å, $c = 5.553$ Å. Weak reflexes at $2\theta = 25°–30°$ (Fig. 1, spectrum *1*) are due to admixed lanthanum oxycarbonate (probably because of some error in the starting stoichiometry with respect to lanthanum). The data of chemical analysis and XRD coincide (Table 1).

*$La_{0.8}Ca_{0.2}FeO_{2.9}$.* According to XRD data, the sample consists of one perovskite phase (Table 1). A small asymmetry of reflexes and their shift toward larger angles are observed (Fig. 1, spectrum *2*), and this may indicate the inclusion of some amount of calcium into the structure of perovskite. However, the shift is very small: $2\theta = 0.02°–0.03°$.

According to the data of differential dissolution, this is a two-phase system (Table 1) consisting of the oxide phases of $La_1Fe_1$ and $Ca_1Fe_1$ partially dissolved in each other. Note that the $Ca_1Fe_1$ phase is neither brownmillerite $Ca_2Fe_2O_5$ (because the reflex from brownmillerite at 7.37 Å is absent) nor $CaFeO_3$ (see JCPDS file #41-753). We suggest that $Ca_1Fe_1O_x$ is a perovskite-like phase with the parameters close to those of lanthanum ferrite. The stabilization of calcium ferrite in the form of a perovskite-like structure can be, for example, due to the microdomain structure of this mixed oxide (similar assumptions have been made in [6]). On the other hand, the calcium ferrite phase can be amorphous.

*$La_{0.6}Ca_{0.4}FeO_{2.8}$.* According to the XRD data, the main phase in this sample is perovskite (Fig. 1, spectrum *3*). Along with the signals from perovskite, a set of reflexes is found, which can be assigned to both brownmillerite and the Grenier phase. The presence of a superstructural reflex at 11.3 Å points to the presence of the Grenier phase, $La_{0.33}Ca_{0.67}FeO_{2.67}$, with the parameters $a = 5.464$, $b = 11.293$, and $c = 5.563$ Å. Thus, according to the XRD data, the sample of this composition consists of the phase with the perovskite structure and the Grenier phase. However, according to

**Table 1.** X-ray phase analysis of the samples

| Sample | La : Ca : Fe according to the chemical analysis* | The XDR data | Content of phases, according to differential dissolution, % |
|---|---|---|---|
| $LaFeO_3$ | 1.1 : 0 : 1.0 | perovskite, $La_2O_2CO_3$ | $La_{1.05}Fe_1$—87<br>La—12 |
| $La_{0.8}Ca_{0.2}FeO_{2.9}$ | 0.81 : 0.18 : 1.0 | perovskite | $La_1Fe_1$—93<br>$Ca_1Fe_1$—5–7 |
| $La_{0.6}Ca_{0.4}FeO_{2.8}$ | 0.66 : 0.37 : 1.0 | perovskite, $La_{0.33}Ca_{0.67}FeO_{2.67}$ | $La_1Fe_1$—70<br>$Ca_1Fe_1$—24<br>La—4 |
| $La_{0.4}Ca_{0.6}FeO_{2.7}$ | 0.45 : 0.54 : 1.0 | perovskite-like phase | $La_{0.5}Ca_{0.54}Fe_1$—95<br>Ca—2<br>Fe—2.7 |
| $La_{0.2}Ca_{0.8}FeO_{2.6}$ | 0.2 : 0.66 : 1.0 | $La_{0.33}Ca_{0.67}FeO_{2.67}$, $CaFe_2O_4$ | $La_{0.3}Ca_{0.8}Fe_1$—84<br>$Ca_1Fe_2$—13<br>La—1<br>Fe—1.5 |
| $Ca_2Fe_2O_5$ | 0 : 0.94 : 1.0 | brownmillerite | $Ca_1Fe_1$—95 |

* Upon complete dissolution of the sample.

the data of the differential dissolution, oxide phases have other stoichiometries ($La_1Fe_1$ and $Ca_1Fe_1$), although the regions of dissolution of these phases are partially overlapped. This can indicate the presence of the X-ray amorphous $CaFeO_x$ phase along with the Grenier phase, because the conditions of dissolution for these oxides are close. In addition, a small amount of lanthanum-containing oxide phase is present.

*$La_{0.4}Ca_{0.6}FeO_{2.7}$.* The band of perovskite on the X-ray diffraction patterns of this sample are split (Fig. 1, spectrum *4*). This splitting could be attributed to the presence of the Grenier phase or brownmillerite, but the reflexes at 11.3 and 7.37 Å corresponding to these phases are absent. On the other hand, according to the data from differential dissolution, this is in fact a single-phase system (only negligible admixtures of starting calcium and iron oxides are present) and its stoichiometry corresponds to the composition $La_{0.5}Ca_{0.54}Fe_1O_x$. The phase of this composition has been theoretically predicted by Grenier in [4] as a member of the homological series with $n = 4$ and the ...OOOTOOOT ... ordering. A period of ~15.5 Å should correspond to this ordering. However, the crystallographic data for the phase of this composition are absent in the literature, and we failed to find the reflex at 15.5 Å. Either the ordering of cations compared to the Grenier model or the complex microdomain structure of the system (similarly to [6]) can be the reason for this phenomenon, which requires further study.

*$La_{0.2}Ca_{0.8}FeO_{2.6}$.* The findings of X-ray analysis and the differential dissolution method give evidence for the formation of the Grenier phase, $La_{0.33}Ca_{0.67}FeO_{2.67}$, and a spinel $CaFe_2O_4$. In addition, the latter method revealed the presence of small amounts of the starting lanthanum and iron oxides. The presence of spinel instead of brownmillerite can be explained by the deficiency of Ca in the starting mixture.

*$Ca_2Fe_2O_5$.* This system is a single-phase (brownmillerite).

Thus, only stoichiometry of the terminal members of a series, $LaFeO_3$ and $Ca_2Fe_2O_5$, corresponds to the expected stoichiometry. This correspondence is absent for intermediate compositions. At $x < 0.5$, the $LaFeO_3$ and $CaFeO_x$ phases are the main products, indicating the absence of a continuous series of homogeneous solid solutions in the range of $x$ from 0 to 0.5. At $x > 0.5$, only triple oxides of two types with the stoichiometry of the Grenier phases are formed. The ratio of cations in the $La_{0.4}Ca_{0.6}FeO_{2.7}$ sample is equal to ~0.5 : 0.5 : 1; this corresponds to $n = 4$. In the $La_{0.2}Ca_{0.8}FeO_{2.6}$, this ratio can be evaluated as approximately 0.3 : 0.8 : 1, which may correspond to $n = 3$. Thus, the formation of the phases of a homological series in the range of $x > 0.5$ is confirmed.

*The microstructure of samples.* Let us consider the data of high-resolution electron microscopy.

*$La_{0.8}Ca_{0.2}FeO_{2.9}$.* The sample consists of large (above 1 μm) particles with a well-arranged bulk structure and a thin (50 Å) disordered layer in the form of nanodomains (blocks) on the surface.

*$La_{0.4}Ca_{0.6}FeO_{2.7}$.* There are dense large particles that are not transmitted (a size above 3 μm) in the sample.

*$La_{0.2}Ca_{0.8}FeO_{2.6}$.* This sample contains mainly particles with sizes above 3 μm whose structures are char-

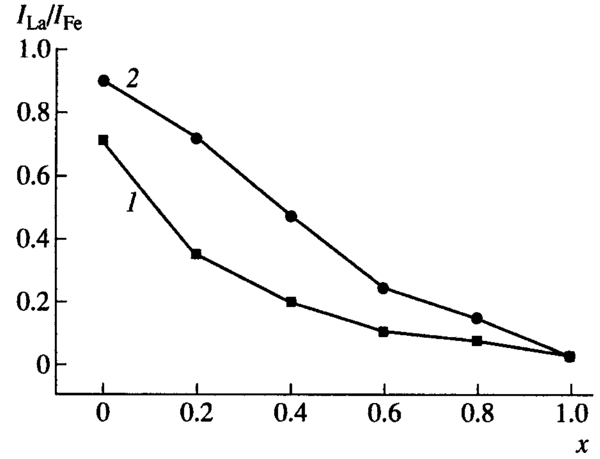

**Fig. 2.** The ratio between the ionic currents of lanthanum-139 and iron-56 in the $La_{1-x}Ca_xFeO_{3-0.5x}$ samples as a function of their chemical compositions at times of bombardment of (*1*) 66 and (*2*) 1000 s.

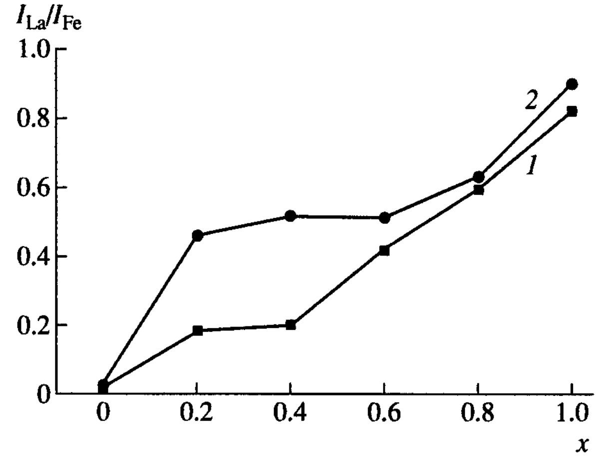

**Fig. 3.** The ratio between the ionic currents of calcium-40 and iron-56 in the $La_{1-x}Ca_xFeO_{3-0.5x}$ samples as a function of their chemical compositions at times of bombardment of (*1*) 1000 and (*2*) 66 s.

acterized by the presence of a number of twinned microdomains with a superstructural period of 11.3 Å. Sometimes, nanosize regions with a disordered structure and size of ~100 Å are observed on the surface of these particles. Submicron particles with a good crystalline internal structure and smooth surface without steps and defects are also seen.

The data obtained confirm the formation of the Grenier phase with $n = 3$ ($La_{0.33}Ca_{0.67}FeO_{2.67}$) and the ...OOTOOT... order and allow one to explain the variations in the findings of the differential dissolution and XRD methods for the sample with $x = 0.2$. The absence of the second phase, $CaFeO_x$, according to the XRD data can be due to the small sizes of its crystallites or structure disordering. In addition, calcium ferrite was shown to be located on the surface of lanthanum ferrite.

Comparing the particle sizes with the specific surface area of the samples (Table 2), one can conclude that the samples do not possess the internal porosity.

*The surface and bulk compositions of samples.* The study of the catalyst composition by SIMS showed that the ratios of ionic currents ($^{40}Ca/^{56}Fe$ and $^{139}La/^{56}Fe$) as functions of both surface and bulk ratios of the lanthanum/iron and calcium/iron concentrations do not change additively in all the samples (Figs. 2, 3). The data divide the samples into two series: $x < 0.5$ and $x > 0.5$. This is due to the difference in the crystalline structure of the samples and consequently to the difference in the sensitivity coefficients in these series, which can result in nonadditivity. One can also conclude that the surfaces of the $La_{0.8}Ca_{0.2}FeO_{2.9}$ and $La_{0.6}Ca_{0.4}FeO_{2.8}$ samples are enriched in calcium cations at a constant iron content; this indicates the surface location of calcium ferrite.

Thus, although according to the XRD data, the samples $LaFeO_3$, $La_{0.8}Ca_{0.2}FeO_{2.9}$, $La_{0.6}Ca_{0.4}FeO_{2.8}$, $La_{0.4}Ca_{0.6}FeO_{2.7}$, $La_{0.2}Ca_{0.8}FeO_{2.6}$, and $Ca_2Fe_2O_5$ synthesized by the ceramic process are in fact single-phase (perovskite at $x < 0.5$, distorted perovskite at $x = 0.5$, and the Grenier phase or brownmillerite at $x > 0.5$), the disagreement of these data with those of differential dissolution indicates that at $x < 0.5$, both true perovskite-based solid solutions and homological series of the phases are not formed. One can affirm that the compositions with $x < 0.5$ in the series of perovskites considered do not form a continuous series of homogeneous solid solutions as believed previously. The systems are two-phase and their particles consist of a well-crystallized center with a perovskite structure and calcium ferrite in the form of nanoparticles located on the surface of lanthanum ferrite. An increase in the calcium content in the system results in the formation of the Grenier phase on the basis of brownmillerite, and the Grenier

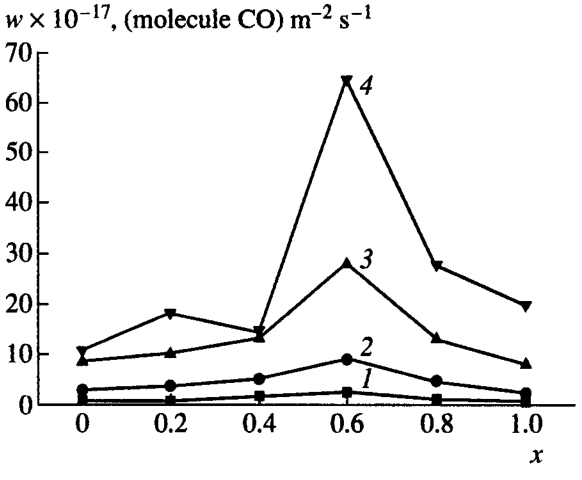

**Fig. 4.** The specific catalytic activity of the $La_{1-x}Ca_xFeO_{3-0.5x}$ samples in the CO oxidation reaction as a function of their chemical compositions at temperatures, °C: (*1*) 300, (*2*) 400, (*3*) 450, and (*4*) 500.

**Table 2.** The specific surface area of the samples prepared

| Sample | Specific surface area, $m^2/g$ |
|---|---|
| $LaFeO_3$ | 2.0 |
| $La_{0.8}Ca_{0.2}FeO_{2.9}$ | 0.7 |
| $La_{0.6}Ca_{0.4}FeO_{2.8}$ | 0.9 |
| $La_{0.4}Ca_{0.6}FeO_{2.7}$ | 0.16 |
| $La_{0.2}Ca_{0.8}FeO_{2.6}$ | 0.4 |
| $Ca_2Fe_2O_5$ | 0.5 |

phase is also located on the surface of the lanthanum ferrite particles. At $x > 0.5$, the Grenier phase with $n = 3$ is formed. At $n = 0.5$, another member of the homological series with $n = 4$ is found whose structure and microstructure need further study.

*Catalytic activity.* The catalytic activity of the perovskites of this series in carbon monoxide oxidation depends nonmonotonically on the calcium content. The activity maximum at the $La_{0.4}Ca_{0.6}FeO_{2.7}$ composition (Fig. 4) is likely due to the formation of the phase with $n = 4$ of a homological series ($La_{0.5}Ca_{0.5}FeO_{2.75}$) whose structure is a transition from perovskite to brownmillerite; this phase possibly consists of alternating blocks of these phases. One can assume that the coordinatively unsaturated active sites, which determine the enhanced catalytic activity of this sample, are formed in the vicinity of the outcrop of the microblocks boundaries to the surface.

Thus, the substitution of lanthanum for calcium in lanthanum ferrite does not result in the formation of the continuous series of homogeneous solid solutions based on the perovskite structure. The systems with $x < 0.5$ are two-phase and consist of lanthanum ferrite and calcium ferrite; the latter is located on the surface of the lanthanum ferrite particles in the form of a layer of nanoblocks. At $x > 0.6$, the system is also two-phase, but it consists of the Grenier phase ($n = 3$) and a spinel. Although the $La_{0.5}Ca_{0.5}FeO_{2.75}$ formula corresponds to the composition of the member of a homological series with $n = 4$, the XRD reflexes do not correspond to the lattice parameters that have been found by Grenier for this phase. Estimates of the parameters for this phase and its morphology will shed light on the enhanced catalytic activity of the sample with the above composition.

## ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 96-03-33103).

## REFERENCES

1. Yamazoe, V. and Teraoka, J., *Catal. Today,* 1990, vol. 8, p. 175.
2. Wu, Y., Yu, T., Dou, B., *et al., J. Catal.,* 1989, vol. 120, p. 88.
3. Grenier, J.-C., Pouchard, M., and Hagenmuller, P., *Structure and Bonding,* Berlin: Springer, 1981, vol. 47, p. 1.
4. Grenier, J.-C., Darriet, J., Pouchard, M., and Hagenmuller, P., *Mat. Res. Bull.,* 1976, vol. 11, p. 1219.
5. Rao, C.N.R., Gopalakrishnan, J., and Vidyasagar, K., *Indian J. Chem., Sect. A,* 1984, vol. 23, p. 265.
6. Alario-Franco, M.A., Conzalez-Calbet, J.M., Vallet-Regi, M., and Crenier, J.C., *J. Solid State Chem.,* 1983, vol. 49, p. 219.
7. Tsybulya, S.V., Kryukova, G.N., Isupova, L.A., *et al., Zh. Strukt. Khim.,* 1998, vol. 39, no. 1, p. 92.
8. Isupova, L.A., Sadykov, V.A., Tsybulya, S.V., *et al., React. Kinet. Catal. Lett.,* 1997, vol. 62, no. 1, p. 129.
9. Isupova, L.A., Sadykov, V.A., Ivanov, V.P., *et al., React. Kinet. Catal. Lett.,* 1994, vol. 55, no. 1, p. 223.
10. Malakhov, V.A. and Vlasov, A.A., *Kinet. Katal.,* 1995, vol. 36, no. 4, p. 503.