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Dynamics of Structural Transformations in the Reduction of Copper Aluminate

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Abstract—The dynamics of structural transformations during copper aluminate reduction in the temperature range used for catalyst activation was studied by high-temperature X-ray analysis under controlled conditions (hydrogen, 20–400°C). The techniques of neutron diffraction analysis, IR spectroscopy, chemical phase analysis, and electron microscopy were also used at particular stages. In the course of reduction, copper metal is deposited onto the surface of spinel crystals from the bulk. Spinel becomes cation-deficient with respect to copper. An analysis of powder diffraction patterns demonstrated that copper is reduced and released from tetrahedral positions of the spinel structure at temperatures below ~300°C and from octahedral positions only at temperatures above 300°C. In this case, a redistribution of aluminum ions was observed simultaneously. It is likely that the electrical neutrality is attained by the formation of OH groups, the appearance of which in reduced samples was detected by IR spectroscopy and confirmed by neutron diffraction analysis. At a reduction temperature of 400°C, the oxygen framework was partially disintegrated. The structures of reduced copper aluminates and chromites were compared.

INTRODUCTION

Compounds with the spinel structure are widely used as catalysts or catalyst components in various processes. For a number of reactions, these catalysts are preactivated with hydrogen. With the use of copper chromite as an example, it has been found that the catalytic properties of spinel in acetone hydrogenation depend on the temperature of catalyst reduction [1].

In this work, we examined the dynamics of structural transformations in the course of reduction of copper aluminate in the temperature range used for catalyst activation.

EXPERIMENTAL

Copper aluminate $CuAl_2O_4$ was prepared by thermal decomposition of copper–aluminum carbonate hydroxide in air at 900°C. The carbonate hydroxide was prepared by coprecipitation from metal nitrate solutions at constant pH and temperature.

X-ray diffraction studies were performed on a Siemens D 500 diffractometer using monochromated CuK_α radiation (a graphite monochromator for the reflected beam). A chamber mounted on the diffractometer and connected to a gas system was used for high-temperature studies [2]. The *in situ* procedure for obtaining X-ray diffraction patterns and data processing with the use of the Polikristall program package were described in detail elsewhere [3].

Studies by other techniques were performed in air at room temperature immediately after the treatment of samples with hydrogen. According to X-ray diffraction data, there is no principal difference in the phase composition of reduced samples determined *in situ* and immediately after contact with air. Copper was gradually oxidized after long exposure in air.

The fragmentary empirical formulas (without oxygen) and the quantities of individual phases in test samples were determined using chemical phase analysis by selective dissolution. The precision of the phase analysis by selective dissolution was ±5 rel %. The analysis was performed in a flow reactor on a setup described in [4]. An inductively coupled plasma atomic emission spectrometer operated in a polychromator system was used as an analyzer detector. Under the dynamic conditions of selective dissolution, the solvent composition was linearly changed from H_2O to a 1.2 M HNO_3 solution and then to an HF solution (1 : 5). In this case, the solvent temperature increased from 60 to 80°C.

The electron-microscopic investigation was performed with a JEM-2010 electron microscope with the linear resolution 1.4 Å.

The IR absorption spectra of samples at 100–4000 cm^{-1} were measured on Bruker IFS-113 and Bomem MB 102 Fourier spectrometers. The samples were prepared as suspensions in fluorinated oil or pressed as CsI pellets. To interpret the IR spectra in the absorption regions of water and hydroxyl groups, samples were deuterated in autoclaves, which were placed in an oven, at 200°C for 20 h.

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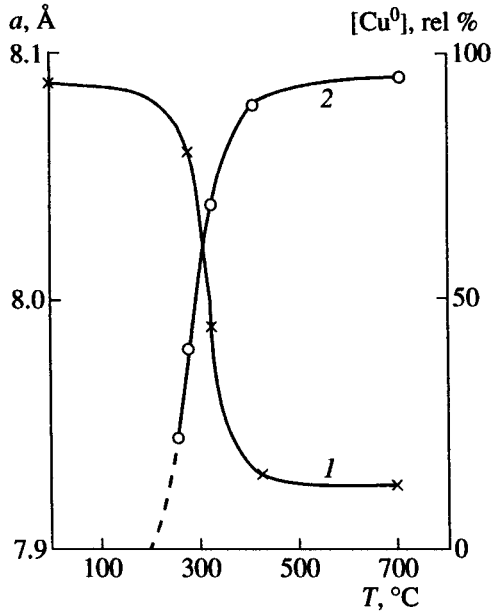

Fig. 1. (*1*) Lattice parameter of copper aluminate and (*2*) the amount of reduced copper as functions of the temperature of reduction.

The neutron diffraction studies were performed on a high-resolution Fourier diffractometer mounted on an IBR-2 pulsed high-flux neutron source at the Joint Institute for Nuclear Research in Dubna. Copper aluminate samples were reduced with hydrogen in a flow reactor at 400°C for 3 to 4 h; the hydrogen flow rate was 2 l/h. After the reduction, the samples were cooled in a flow of hydrogen. Before performing a neutron diffraction experiment, a sample was placed in a special container positioned on the high-resolution Fourier diffractometer. The cylindrical containers 5 mm in diameter were made of a Ti–Zr alloy with the zero length of coherent scattering to prevent the appearance of additional peaks in neutron diffraction patterns. The MRIA program was used for the treatment of neutron diffraction data by the Rietveld method [5]. The refinement of structure parameters was performed by Fourier spectra in the d_{hkl} range from 0.6 to 2.2 Å, which contains about 40 diffraction peaks, using a model based on the cubic spinel structure.

RESULTS AND DISCUSSION

Phase composition of samples in a hydrogen atmosphere. According to X-ray diffraction data, the initial sample was copper aluminate $CuAl_2O_4$ with the spinel structure and a lattice parameter close to the tabulated value (a = 8.085 and 8.086 Å [6], respectively) (Table 1). The CuO phase was also detected in trace amounts (~1–1.5 wt %). A study performed by *in situ* high-temperature X-ray diffraction in a hydrogen atmosphere revealed no detectable changes in the diffraction patterns up to ~200°C. As the temperature was further increased, a copper metal phase appeared; the amount of this phase increased very rapidly at 300–400°C (Figs. 1, 2) and was as high as 70–80% (with respect to the copper content of spinel) at 400°C. In the temperature range 400–700°C, the amount of metallic copper increased more slowly and did not reach 100% even at 700°C. Although copper was liberated, generally, the spinel structure was retained up to 700°C. However, as the temperature was increased, a redistribution of the intensities of spinel diffraction lines was observed in the diffraction patterns, and the lines shifted relatively to those of the initial sample (Fig. 2a).

Let us consider the results of chemical phase analysis. Figure 3 demonstrates typical curves obtained by the selective dissolution of the phases of copper aluminate reduced at 320°C. It follows from Fig. 3 that this sample contains three phases with the fragmentary formulas Cu, $Cu_{0.34}Al_2$, and $CuAl_2$. A comparison between the data of selective dissolution and the results of X-ray diffraction analysis, which are summarized in Table 1, can show whether these phases are metal or oxide and what structure they exhibit. The initial sample primarily contains a phase of the composition $CuAl_2$ and

Table 1. XRD and selective dissolution data on phase composition of reduced copper aluminate

Sample	According to XRD*	Phase composition, wt % (according to selective dissolution data)				
		CuO	Al_2O_3	$CuAl_2O_4$	Cu^0	Cu–Al phase
$CuAl_2O_4$ (initial)	Spinel + trace CuO (8.085)	1.20	3.30	95.5	–	–
Reduced at 270°C	Spinel + Cu^0 (8.060), 30	–	–	–	–	–
Reduced at 320°C	Spinel + Cu^0 (7.990), 60	–	–	4.40	20.8	74.8 ($Cu_{0.34}Al_2$)
Reduced at 400°C	Spinel + Cu^0 (7.931), 85	–	–	3.00	29.1	67.9 ($Cu_{0.12}Al_2$)
Reduced at 700°C	Spinel + Cu^0 (7.925), 90	–	–	2.20	30.4	67.4 ($Cu_{0.10}Al_2$)

* Parenthesized figures indicate the a parameter (Å), and the other figures indicate the Cu^0 content (rel %).

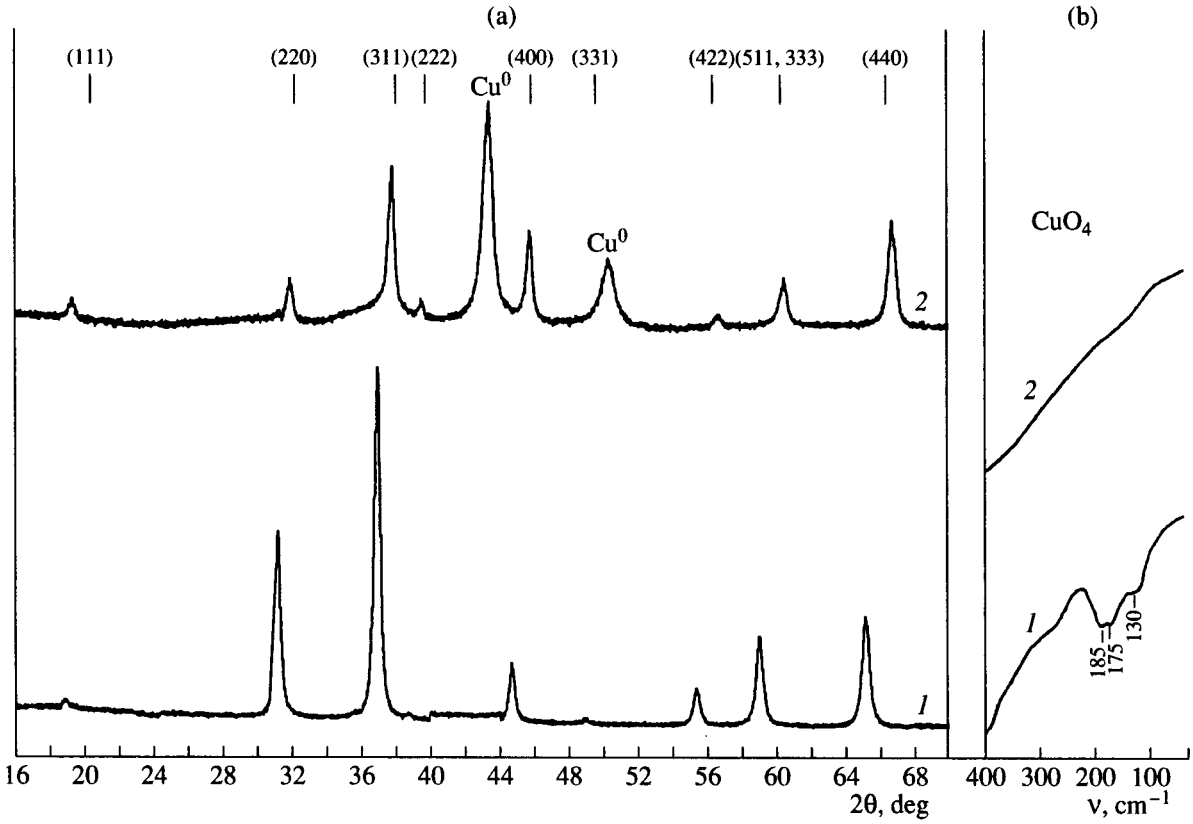

Fig. 2. (a) X-ray diffraction patterns and (b) IR spectra of (*1*) the initial sample and (*2*) copper aluminate reduced at 400°C.

small amounts of copper and aluminum. The phase composition was changed as a result of reduction: the amount of free copper increased, a copper–aluminum phase of variable composition appeared, and small amounts (<5%) of the $CuAl_2$ phase were retained. At 400–700°C, the phase composition changed only slightly.

The use of selective dissolution allowed us to detail the phase composition. We found the stoichiometry of phases of variable composition and detected small amounts of aluminum oxide (that does not enter the aluminate) or copper aluminate (unreacted with hydrogen), which cannot be detected by X-ray diffraction (it is difficult to distinguish small amounts of phases with similar lattice parameters against a background of the main phase).

It follows from the set of data obtained that, in the reaction of copper aluminate with hydrogen, gradual release of copper metal from spinel rather than decomposition to form copper metal and aluminum oxide occurred. Cation-deficient spinel with respect to copper was formed, whose composition was changed as copper was released. The formation of cation-deficient spinels stabilized by absorbed hydrogen has been observed previously in the study of the interaction of hydrogen with copper chromite [1].

Let us consider the special features of phases formed upon the reduction.

Copper metal phase. Figure 4 shows the micrographs of test samples. The initial copper aluminate

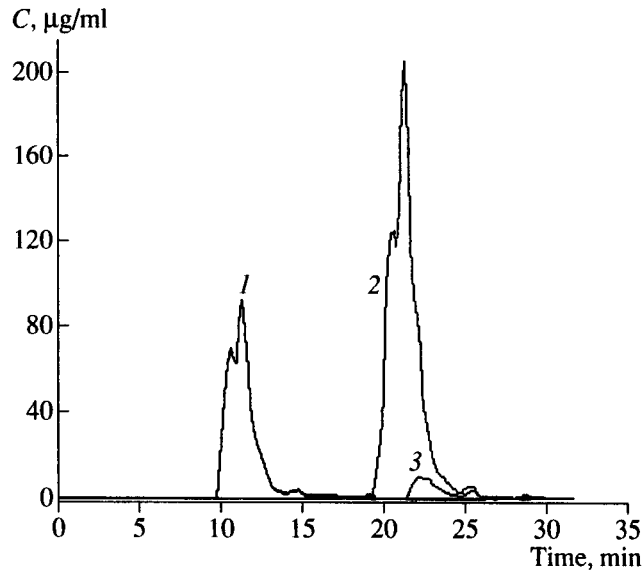

Fig. 3. Curves of the selective dissolution of phases in a copper aluminate sample reduced at 320°C: (*1*) Cu^0, (*2*) $Cu_{0.34}Al_2O_{4-x}$, and (*3*) $CuAl_2O_4$.

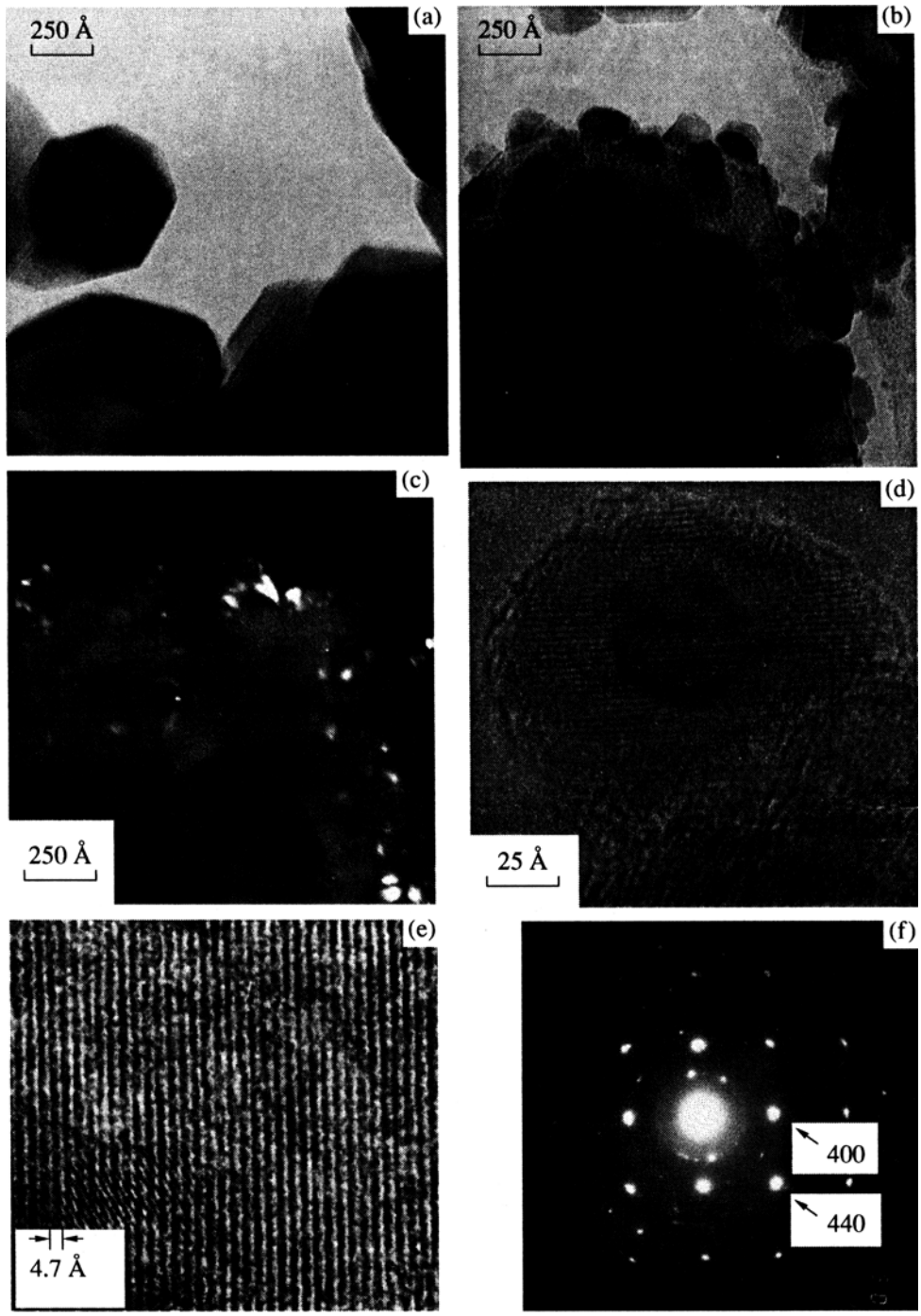

Fig. 4. Micrographs of the initial copper aluminate and copper aluminate reduced at 400 °C: (a) initial copper aluminate, (b) copper aluminate after reduction at 400°C (bright-field image), (c) the same sample (dark-field image), (d) copper particles with an oxide layer at the surface of reduced copper aluminate crystals, (e) direct resolution of the lattice of a porous crystal of reduced copper aluminate, and (f) microdiffraction pattern of a reduced porous crystal of copper aluminate, [001] zone.

exhibits well-faceted isometric particles of size 500–1000 Å (Fig. 4a). The reduced aluminate exhibits spherical particles of size 50–200 Å, which are adjacent to the faces of coarse crystals (Fig. 4b). According to the data of electron diffraction microscopy (Fig. 4f), the fine hemispherical and coarse particles are metallic copper and a phase with the spinel structure, respectively. The particles of Cu^0 are randomly oriented to the surface, as can be seen in the dark-field image obtained in the Cu(111) beam (Fig. 4c). As can be seen in Fig. 4d, copper metal particles are single crystals, the surface of which is coated with a thin oxide film (because of contact with air). As the temperature of reduction was increased to 400°C, the amount of copper particles of

Table 2. Structural characteristics of $CuAl_2O_4$ reduced at different temperatures

T, °C, and atmosphere	Structural formula and cation distribution in spinels*	Oxygen parameter x***	R****, %
900, air	$[Cu_{0.60}Al_{0.40}]^{8a}[Cu_{0.20}Al_{0.80}]_2{}^{16d}O_4$	0.3841(5)	4.4
	$[Cu_{0.60}Al_{0.40}]^{8a}[Cu_{0.20}Al_{0.80}]_2{}^{16d}O_4$**	0.3866(1)	6.4
270, H_2	$[Cu_{0.23}Al_{0.79}]^{8a}[Cu_{0.20}Al_{0.62}]_2{}^{16d}O_{3.35}OH_{0.65}$	0.3808(5)	5.6
320, H_2	$[Al_{0.84}]^{8a}[Cu_{0.16}Al_{0.58}]_2{}^{16d}O_{2.64}OH_{1.36}$	0.3790(3)	7.2
400, H_2	$[Al_{0.83}]^{8a}[Cu_{0.05}Al_{0.70}]_2{}^{16d}O_{2.88}OH_{1.12}$	0.3777(3)	4.5
	$[Al_{0.85}]^{8a}[Cu_{0.05}Al_{0.70}]_2{}^{16d}O_{3.17}OH_{0.64}$**	0.3794(2)	9.1

* The superscripts 8a and 16d refer to the tetrahedral and octahedral positions, respectively, in the spinel structure.

** According to neutron diffraction data.

*** Coordinates of oxygen atoms that occupy the 32*e* crystallographic positions with coordinates (x, x, x) in the structure of spinel (space group *Fd3m*).

**** The divergence factor for the experimental and simulated diffraction patterns.

size 50–200 Å at the spinel surface gradually increased. At temperatures higher than 400°C, the particles were partially separated from the spinel surface and agglomerated.

Spinel phase. As noted above, heating in a hydrogen flow resulted in the formation of cation-deficient spinels with respect to copper. The X-ray diffraction patterns of these spinels are different from that of $CuAl_2O_4$ (see Fig. 2a). Figure 1 (curve *1*) demonstrates the lattice parameter of copper aluminate as a function of reduction temperature. A comparison of curves *1* and *2* in Fig. 1 shows that the lattice parameter of copper aluminate and the relative amount of copper released from spinel exhibit opposite patterns of change. Note that the lattice parameter of the spinel phase at 700°C (a = 7.925 Å) is close to the corresponding parameters of low-temperature alumina species (γ-Al_2O_3, a = 7.90–7.92 Å [7]). However, the intensity distribution and the profile of diffraction lines are different from those typical of low-temperature aluminum oxides with the spinel structure.

An analysis of peak broadening in the diffraction patterns of the test samples is indicative of the absence of extensive defects (like displacement of layers and stacking faults) and size anisotropy. An analysis of reflection pairs (220/440) by the Warren–Averbach method [8] demonstrated that, upon the reduction, the size of coherent-scattering regions changed only slightly; however, the dimensions of microdefects increased. Thus, the size of the coherent-scattering region for the $CuAl_2O_4$ sample reduced at 270°C increased by 10% (500 Å versus 450 Å for the initial sample), and the size of microdefects increased by a factor of 2 (0.0004 and 0.0002, respectively).

Table 2 summarizes the results of examining the samples by structure refinement using powder data. This technique allowed us to determine the cationic composition and the distribution of Cu and Al ions over individual crystallographic positions in the structure of copper aluminate reduced at 270, 320, and 400°C. In general, the X-ray diffraction data on the cationic composition of reduced spinels are in good agreement with the fragmentary formulas of Cu–Al phases found by the method of selective dissolution (cf. Tables 1, 2). Moreover, additional information on the distribution of cations was obtained.

The above data indicate that copper aluminate in the initial sample is partially inverted; this is consistent with the published data [6]. As the reduction temperature was increased, the cationic composition of spinel changed: the amount of copper ions decreased; moreover, the number of aluminum ions per formula unit increased at 400°C (see Table 2). At temperatures below ~300°C, copper ions located at the tetrahedral positions of the spinel structure were reduced, and the reduction of copper ions occupying the octahedral positions began at a higher temperature. This result was also supported by the IR data. Figure 2b shows the vibrational bands of the $[CuO_4]$ group for the initial aluminate (ν = 130, 175, and 185 cm^{-1}); these bands are absent from the spectrum of the sample reduced at 320°C. Note that a redistribution of Al^{3+} ions occurred simultaneously with the release of copper.

In samples reduced at 400°C, the number of aluminum ions per formula unit is higher than 2 (generally, it is equal to 2.23). This fact is indicative of partial disintegration of the oxygen framework of the spinel structure and of the removal of oxygen as H_2O. In these samples, spinel crystals occupy the same volume but become porous; at the same time, they are still single crystals. This is evident from the data of electron microscopy and by the point pattern of electron diffraction microscopy (Figs. 4b, 4e, and 4f). It is likely that this microstructure results from the release of copper ions and lattice oxygen. In this case, the remaining part of the structure in the bulk of the crystal retained a single oxygen framework, although having lattice vacancies and distortions (defects), as mentioned above.

An analysis of the electrostatic balance of structural formulas given in Table 2 demonstrates that the reduced aluminates are deficient in positive charges for the electrical neutrality on a basis of the spinel formula AB_2O_4.

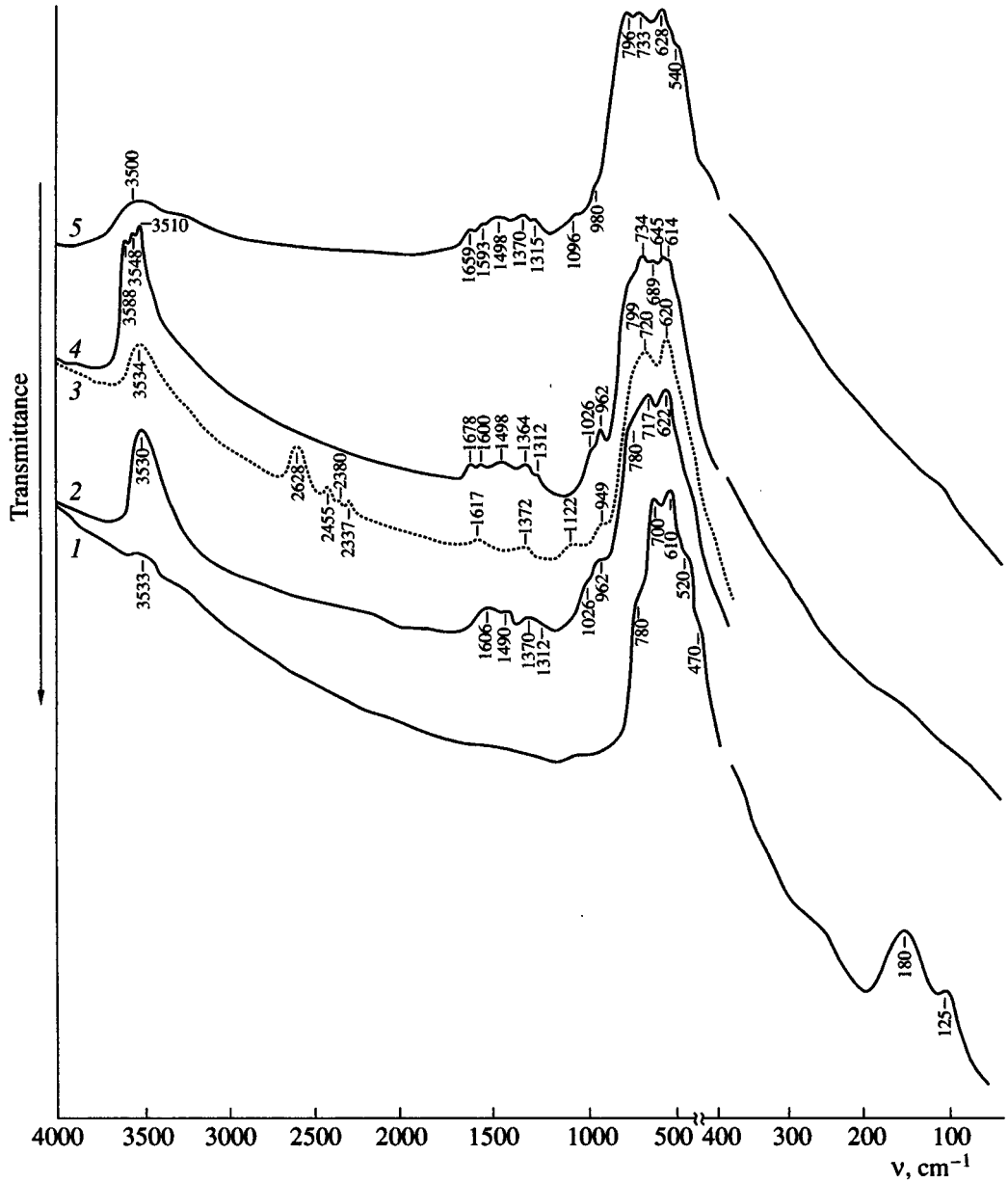

Fig. 5. IR spectra of (*1*) the initial copper aluminate sample and samples reduced at the following temperatures, °C: (*2*) 300 (hydrogen), (*3*) 350 (deuterium), (*4*) 350 (hydrogen), and (*5*) 400 (hydrogen).

The deficient charges can be compensated by the replacement of a portion of oxygen ions with OH groups resulting from the reduction of copper ions in the bulk of aluminate crystals. Table 2 summarizes the calculated numbers of O^{2-} and OH^- in the anionic frameworks of cation-deficient spinels.

The ability of copper aluminate to absorb hydrogen is well known [9]. However, there is no detailed data on hydrogen species and location in this structure. To elucidate this problem, we performed IR-spectroscopic and neutron diffraction studies.

Figure 5 shows the IR spectra of samples in the frequency range 300–4000 cm^{-1}. A comparison between the IR spectra of the initial aluminate and the aluminate reduced at 300°C (Fig. 5, spectra *1*, *2*) demonstrates that additional adsorption bands at 962, 1026, 1312, 1370, 1490, and 1606 cm^{-1} appeared after reduction. The absorption band at 3530 cm^{-1} became much more intense than that in the spectrum of the initial sample. The absorption bands at 3530 and 1606 cm^{-1} were assigned to stretching and deformation vibrations of water molecules, respectively [10]. According to [11], the absorption band at 962 cm^{-1} is typical of deformation vibrations of the Al–O–H angles in AlO_4 tetrahedrons. The absorption band at 1026 cm^{-1} can be interpreted as a result of deformation vibrations of the

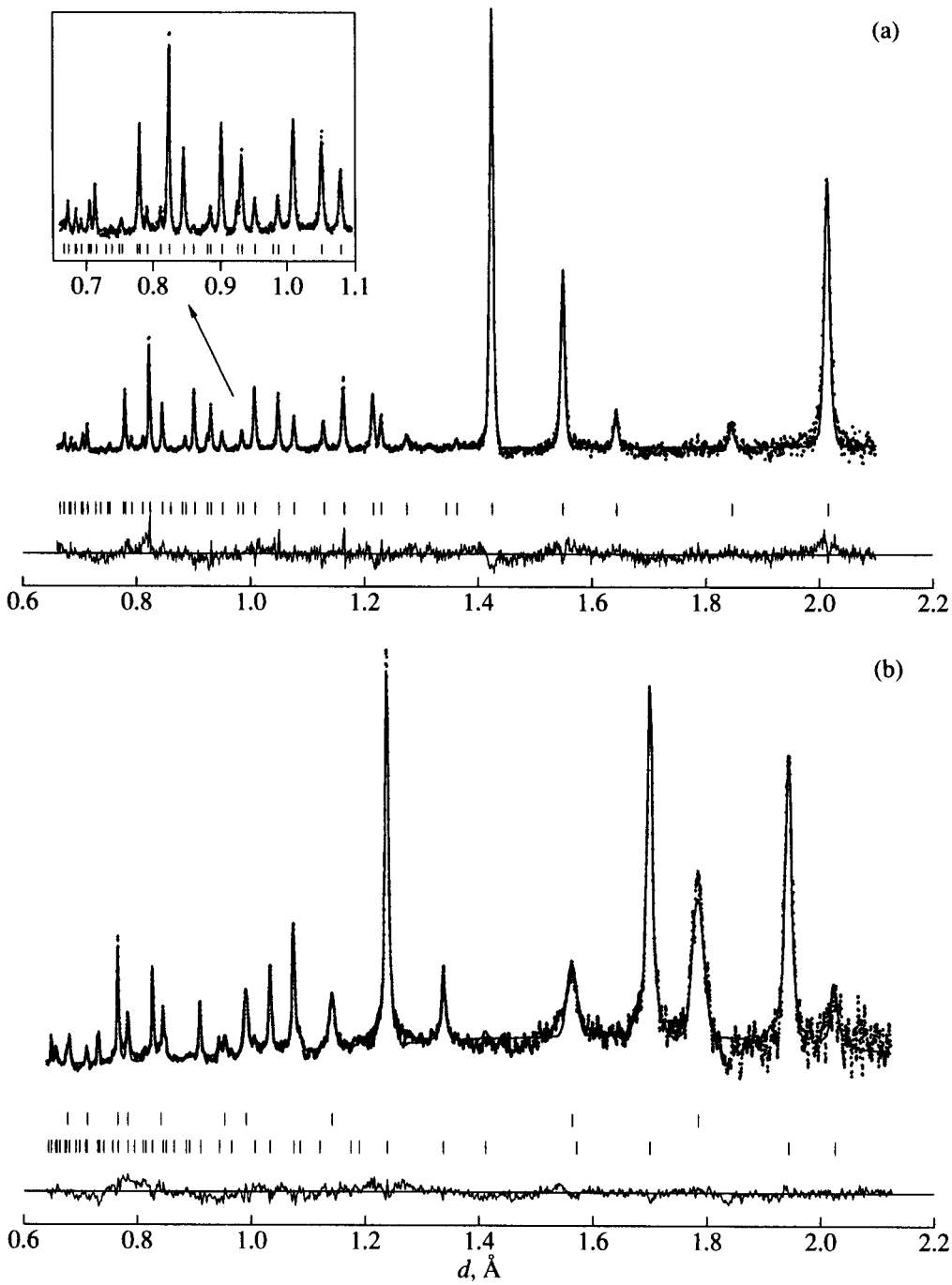

Fig. 6. (a) Diffraction spectrum of initial $CuAl_2O_4$ measured on a high-resolution Fourier diffractometer (bottom) and the result of its treatment by the Rietveld method (top). The difference curve was normalized to the root-mean-square deviation at point ($\chi^2 = 2.2$). (b) Analogous data for copper aluminate reduced at 400°C ($\chi^2 = 1.82$).

hydroxyl group that forms a bridge between two metal atoms [12]. The samples reduced at 350 and 400°C exhibited analogous spectra.

To interpret the absorption band of OH groups more adequately, a sample reduced at 300°C was subjected to deuterium exchange. The IR spectrum of the deuterated sample (Fig. 5, spectrum *3*) exhibits a decrease in the absorption at 3530 cm^{-1}; the absorption bands due to D_2O at 2628 cm^{-1} and due to OD groups at 2455, 2380, and 1337 cm^{-1} appeared [10]. Analogous IR bands of OH groups should correspond to the above bands; however, they are hidden because of a broad absorption band in the region at 3530 cm^{-1}. Moreover, an absorption band at 1490 cm^{-1} disappeared, and a new band appeared at 1122 cm^{-1}. The absorption bands at 1026

and 962 cm^{-1} also shifted toward lower frequencies. These changes are indicative of the replacement of OH groups by OD groups and confirm the assignment of IR bands at 1490, 1026, and 962 cm^{-1} to vibrations in the OH group.

Thus, it follows from an analysis of the IR spectra that OH groups are formed in the copper aluminate structure upon reduction in a certain temperature range.

Figure 6 demonstrates the neutron diffraction spectra of the initial copper aluminate and the sample reduced at 400°C; the spectra were measured on a high-resolution Fourier diffractometer and treated by the Rietveld method. Table 2 summarizes the structural formulas found from the neutron diffraction data for the test samples. The copper and aluminum cation distribution found by this technique is in close agreement with the X-ray diffraction data. This fact shows the reliability of the results obtained. Moreover, according to the refinement based on neutron diffraction patterns, the sample reduced at 400°C contained 0.6 ± 0.1 hydrogen atoms statistically distributed over the 32*e* crystallographic positions of space group *Fd3m* with coordinates (x, x, x), where $x = 0.320(3)$. The nearest environment of this hydrogen includes four oxygen atoms arranged as a tetrahedron; one of them is separated by a distance of 0.9 Å, and the other three, by a distance of 2.27 Å. The short distance 0.9 Å indicates that hydrogen is covalently bonded to the lattice oxygen. The decreased number of oxygen atoms per formula unit indicate the partial disintegration of the oxygen framework of spinel.

The ratio between O^{2-} and OH^- found here is somewhat different from the calculated value (Table 2). This is probably because the degree of disintegration of the anionic framework was not taken into account in these calculations. Generally, the neutron diffraction data indicate the presence of OH groups in the oxygen framework of cation-deficient aluminates with respect to copper.

Thus, we can suggest that during the interaction of hydrogen with copper aluminate (as with copper chromite [3]) hydrogen is absorbed in the bulk of spinel crystals. Dissolved hydrogen reacts with copper ions to reduce copper to a zero-valent state. Copper atoms form hemispherical particles at the surface of cation-deficient aluminate. The resulting protons bind to the lattice oxygen and remain in the structure as OH groups stabilizing the structure. As the temperature increases, a fraction of hydrogen also reacts with the lattice oxygen to form water molecules. In this case, metallic copper is also formed, and the spinel loses a portion of oxygen; as a result of this, the crystals become porous, and irreducible aluminum ions diffuse into the residual oxygen framework.

A comparison between the structures of reduced copper aluminate and copper chromite [3] demonstrates that first tetrahedrally coordinated and then octahedrally coordinated copper ions leave both structures. Copper metal particles form crystals at the surface of spinel crystals. However, in the case of the chromite, copper particles are epitaxially bonded to the surface of cation-deficient spinel, whereas this bond does not occur in the aluminate. The oxygen framework of the reduced copper chromite is stable up to 380–400°C, and Cr^{3+} ions occupy octahedral positions at all temperatures. The cation-deficient chromite with respect to copper is stabilized by the formation of OH groups as a result of the interaction between protons and lattice oxygen. These OH groups are concentrated in copper-free tetrahedrons. This provides local compensation for a deficient positive charge. In this case, extended defects like displacement of layers in the [111] direction are formed in the structure. In the reduced copper aluminate, the oxygen framework begins to disintegrate at a lower temperature, and Al^{3+} ions migrate throughout the structure and also occupy a part of tetrahedral positions that became free as a result of the copper escape. The absorbed hydrogen reacts not only with copper ions to form OH groups but also with the lattice oxygen to form water; this causes the initial crystal to become porous. These differences can be responsible for different catalytic properties of copper chromite and copper aluminate.

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