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Interaction of Hydrogen with Copper-Containing Oxide Catalysts: V. Structural Transformations in Copper Chromite during Reduction–Reoxidation

L. M. Plyasova, I. Yu. Molina, T. A. Kriger, L. P. Davydova,
V. V. Malakhov, L. S. Dovlitova, and T. M. Yur'eva
Boreskov Institute of Catalysis, Siberian Division,
Russian Academy of Sciences, Novosibirsk, 630090 Russia
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Abstract—High-precision X-ray powder diffraction and differential dissolution methods are used to show that copper chromite with a structure of tetragonal spinel is recovered under certain conditions upon the reoxidation of the system of phases formed by the reduction of the initial copper chromite, cation-deficient spinel stabilized by hydrogen and Cu^0 particles epitaxially bound to its surface at 250–350°C. However, because of destruction of the initial surface layer at the initial moment of reduction, equilibrium cannot be complete: reoxidized spinel is nonstoichiometric and contains some lattice oxygen-bound protons, and the copper oxide is formed on the surface in some amount. The difference in the phase transition of copper chromite during reduction–reoxidation from the reversible polymorphic transitions characteristic of copper chromite during temperature variations is analyzed.

INTRODUCTION

Copper-containing catalysts are widely used in many processes occurring in the reductive media. Various hydrogenation catalysts consume hydrogen in the course of their activation [1, 2]. When elucidating the mechanism of their catalytic action, it is necessary to study the properties of hydrogen consumed. Copper chromite is very interesting from this standpoint because its reaction with hydrogen leads to structural changes in the bulk, and these changes can be studied by diffraction methods.

Makarova *et al.* [2] showed by *in situ* X-ray analysis that the interaction of copper chromite with hydrogen at 180–350°C does not lead to the destructive transformation of spinel. The study of low-temperature reduction by the kinetic method [3] with the monitoring of hydrogen consumption and water formation showed that only surface oxygen of copper chromite reacts with hydrogen to form water and that the main reduction is not associated with chromite destruction. Detailed structural studies by the methods of powder X-ray and neutron diffraction analysis [4, 5] allowed us to conclude that the reduction of copper chromite by hydrogen at these temperatures results in the redox substitution of Cu^{2+} ions in oxygen tetrahedrons of spinel by protons and the formation of (1) Cu^0 species epitaxially bound to the surface of cation-deficient spinel and (2) Cu^{1+} ions in oxygen octahedrons of spinel. Also, some portion of hydrogen is distributed between the nodes of octahedrons as neutral atoms the presence of which is not associated with the valence transition of copper. Under some reoxidation conditions, Cu^0 and Cu^{1+} transform back to Cu^{2+}, and spinel is reconstructed and acquires the structure similar to the initial one. Second reduction under the same condition does not lead to the loss of the capability of reversible changes during reoxidation.

This paper reports on the study of the conditions for the reversible transformations in copper chromite during reduction–reoxidation and analyzes structural changes that accompany these processes, as well as the structure of reoxidized copper chromite.

EXPERIMENTAL

The initial sample of copper chromite was prepared by thermal decomposition of copper–chromium hydroxocarbonate with further calcination at 900°C [2].

This sample was treated with different gases in a flow-type quartz reactor. At the first stage (as in [2]), reduction was carried out with H_2 at 270°C for 3–4 h after which ~50% of spinel copper was reduced. Then, the sample was allowed to stay at 290°C for ~20 h in a helium flow purified or not purified of O_2 traces (0.05 vol %). After each experiment, the sample was cooled to room temperature and studied.

The phase composition of samples was studied by X-ray phase analysis and by differential dissolution [6]. The differential dissolution was used to determine empirical fragmental formulas (without oxygen) and the concentrations of individual phases in the samples. The uncertainty of phase analyses by differential dissolution was ±5%. Analyses were performed in a flow-type reactor in the setup described in [6]. Atom emission spectrometer with inductively bound plasma working in a polychromator system was used as a detector/analyzer. The conditions for the dynamic regime of the differential dissolution implied a linear change in the solvent composition from H_2O to 1.2 mol/l HNO_3 and then to the HF solution (1 : 5). The solvent temperature increased from 60 to 80°C.

To study the structural features of reoxidized copper chromite, we compared the structural characteristics of the initial and reoxidized copper chromite by X-ray data. An URD-63 diffractometer (Germany) was used with a CuK_α monochromatic irradiation. X-ray diffraction patterns were obtained by scanning in the region of angles $2\theta = 15°–140°$ with a 0.02° step and a signal accumulation period of 20 s. To process the experimental data and refine the structures using the complete X-ray diffraction pattern profiles, we used the GSAS program and the Polikristall program package [7].

RESULTS AND DISCUSSION

Phase Composition of Initial, Reduced, and Reoxidized Samples

Figure 1 shows diffraction patterns for the initial (curve *1*) and reduced (curve *2*) samples, as well as for the samples reduced in the medium of an inert gas containing ~0.05% of oxygen (curve *3*) or purified of oxygen (curve *4*). Table 1 describes the phase composition of the samples according to differential dissolution and X-ray phase analysis. The X-ray diffraction data suggest that the initial sample is tetragonal-distorted spinel with a small admixture of α-Cr_2O_3 (Fig. 1, curve *1*). The study of the sample by differential dissolution showed that the concentration of chromium oxide was ~1.5%, and at least 1% of copper oxide was present in addition to chromium oxide. Figure 1 also shows the X-ray pattern of the reduced sample (curve *2*). Its form coincides with that obtained *in situ* under reduction conditions and analyzed in detail in [4, 5]. Based on these data, we concluded that the reduced sample is cubic spinel with a structure stabilized by protons. According to the X-ray and neutron diffraction data, this spinel has the formula $[Cu^{2+}]^{a}_{0.33}[\overset{+}{H}_{0.30}]^{e}_{4}[\overset{+}{Cu}_{0.07}]^{c}_{2}Cr^{d}_{2}O_4$, where a, c, d, and e are crystallographic position of atoms in the structures of spinel. The atomic ratio $Cu^{2+} + Cu^{1+}/Cr^{3+}$ is 0.235. The composition of the reduced sample was confirmed by differential dissolution: the copper-chromium phase has a Cu/Cr ratio of 0.265 (Table 1), although the initial sample contained the spinel phase with a Cu/Cr ratio of 0.5. Therefore, in the reduced sample, ~50% of copper ions transforms into Cu^0. These findings agree with the results reported in [2], where we showed by electron microscopy that ~50% of Cu^{2+} in spinel is reduced to Cu^0 and come out onto the spinel surface. When the reduced sample was treated for 20 h by an inert gas purified of oxygen traces, copper did not return to the spinel structure. Comparison of curves *2* and *4* in Fig. 1 suggests that the diffraction pattern remains virtually unchanged: diffraction lines of cubic spinel and metallic copper are observed. After the treatment of the reduced sample for 20 h in helium containing oxygen admixtures, the diffraction pattern changed (Fig. 1, curve *3*): the phase of metallic copper disappears, and the spinel structure becomes tetrahedron-distorted again. According to the differential dissolution data, the Cu/Cr ratio in reoxidized spinel increased relatively to that in the reduced sample and reached 0.4, although this ratio was 0.5 in the initial sample (Table 1). Therefore, reoxidation did not lead to the complete recovery of the initial sample. The X-ray pattern lines from copper oxide Cu_2O, which were not observed for the initial sample, also point to this fact. According to the differential dissolution data, the amount of copper phase decreased, while the amount of chromium oxide phase remained as in the reduced sample. Comparatively to the initial sample, the amount of copper phase somewhat increased. An increase in the time of sample treatment in a flow of nonpurified helium to 50 h did not lead to substantial changes in the parameters of spinel lattice, but it led to the deeper oxidation of copper in the oxide as follows from the X-ray pattern containing lines from the CuO phase.

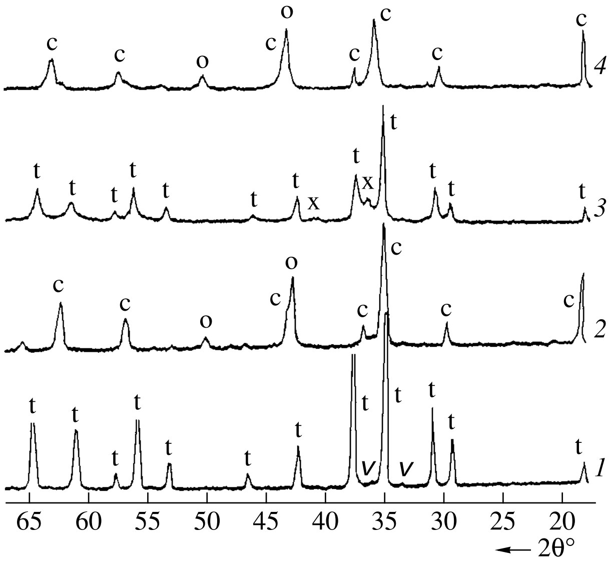

Fig. 1. Diffraction patterns of copper chromite: (*1*) initial sample; (*2*) sample reduced in a hydrogen flow, 270°C; (*3*) after the treatment of the reduced sample in a flow of nonpurified helium, 290°C; and (*4*) after the treatment of the reduced sample in a flow of purified helium, 290°C. Notation: (t) corresponds to tetragonal spinel, (c) corresponds to cubic spinel, (o)—Cu^0, (x)—Cu_2O, and (V)—Cr_2O_3.

When the reduced sample is heated in air to 630°C, metallic copper is completely oxidized to form Cu_2O and/or CuO, and the cation-deficient spinel is decomposed to form Cu(I) chromite and α-Cr_2O_3 (Table 1).

Thus, the above data suggest that copper atoms are oxidized to Cu^{2+} and return to the structure of the chromite with a noticeable rate only in a flow of an inert gas containing oxygen admixtures. Obviously, this process is associated with the interaction of protons that stabilize cation-deficient spinel, but the direct exchange interaction $Cu^0 + 2H^+ \rightleftarrows Cu^{2+} + H_2$ is hampered. Electron transfer from copper to protons is simplified by the intermediate interaction of copper with oxygen via the reaction $2Cu^0 + O_2 + 4H^+ = 2Cu^{2+} + 2H_2O$. An increase in the concentration of oxygen at 290°C favors the rapid oxidation of metallic copper ($2Cu^0 + O_2 = 2CuO$). As a result, copper ions do not return to the structure of spinel, and cation-deficient spinel containing Cu^{1+} ions frees itself from protons by forming water and $CuCrO_2$. The process rate increases with an increase in temperature (see Table 1, reoxidation in air at 630°C).

Comparison between the Structures of Initial and Reoxidized Copper Chromite

The structure of copper chromite was first studied by powder neutron diffraction by Prince in 1957 [8]. In this study, we refined the structure of initial copper chromite using X-ray data.

Table 2 summarizes the results on the refined structure within the framework of the space group I-42d by the method of full-profile analysis. Figure 2a shows the experimental diffraction pattern of initial copper chromite and the pattern calculated using the final model. They show a good agreement. The unit-cell parameters of the initial sample are $a = 6.032$ Å, $c = 7.786$ Å, and $c/a = 1.29$. According to this space group for the tetragonal-distorted spinel, all tetragon positions 4a are occupied by copper ions, and all octahedron positions 8d are occupied by chromium atoms. Oxygen atoms occupy the positions 16e. Analysis of interatomic distances showed that Cu^{2+} ions are surrounded by four oxygen atoms at equal Cu–O distances (1.935 Å). They form a distorted tetrahedron with angles of ~103°, which are somewhat smaller than in a regular tetrahedron (~109°). This probably reflects that copper strives for a characteristic square–planar coordination. The polyhedron is distorted due to the Jahn–Teller effect. Because oxygen tetrahedrons occupied by copper ions in the structure of spinel and octahedrons occupied by chromium atoms have common vertices, the deformation of tetrahedrons results in deformation of octahedrons and shifted chromium positions. As a consequence, three pairs of unequal Cr–O distances appear in the structure (Table 2). The ordered arrangement of distorted polyhedrons in the space results in the appearance of tetragonal-distorted spinel structures.

With an increase in temperature, the thermal motion of atoms results in disordered distortion in polyhedra, and the structure is described as statistically cubic. Tetragonal-distorted copper chromite is known to transform into cubic chromite at 560°C [9]. According to Ust'yantsev and Mar'evich [10], the parameters of cubic and tetragonal cells are related as $a = \sqrt{2}/2A$ and $c = A$, where A is the parameter of a cubic unit cell, and a and c are the parameters of tetragonal unit cell. Figure 3 shows the projection of cubic and tetragonal cells onto the (001) plane. The shifts of oxygen and chromium atoms in tetragonal-distorted unit cells relatively to their equilibrium positions in a cubic unit cell are seen.

Table 1. Phase composition of the $CuCr_2O_4$ sample after different treatments

No.	Sample and treatment	X-ray phase data	Differential dissolution data	
			fragmental formulas	wt %
1	$CuCr_2O_4$	Traces α-Cr_2O_3,	Cu	1.0
	900°C, 4 h, air	$CuCr_2O_4$ (T, $c/a = 1.29$)	Cr	1.3
			Cu_1Cr_2	97.7
2	$CuCr_2O_4$	Cu^0,	Cu	17.3
	270°C, 4 h, H_2 [2, 3]	$CuCr_2O_4$ (C, $a = 8.40$ Å)	Cr	2.4
			$Cu_{0.53}Cr_2$	81.3
3	Sample 2	Cu^0, $CuCr_2O_4$	Cu	~18.0
	290°C, 20 h, He, without O_2	(C, $a = 8.40$ Å)	Cr	~2.4
			$Cu_{0.5}Cr_2$	~79.6
4	Sample 2	Cu_2O,	Cu	4.5
	290°C, 20 h, He with O_2	$CuCr_2O_4$ (T, $c/a = 1.32$)	Cr	2.4
			$Cu_{0.8}Cr_2$	93.1
5	Sample 2	$CuCr_2O_4 + CuCrO_2 +$	–	–
	630°C, air	α-Cr_2O_3 + CuO	–	–

Note: X-ray data: T—tetragonal spinel; C—cubic spinel; Differential dissolution data: Cu + Cr = 100 wt %; fragmental formulas are determined without taking into account oxygen.

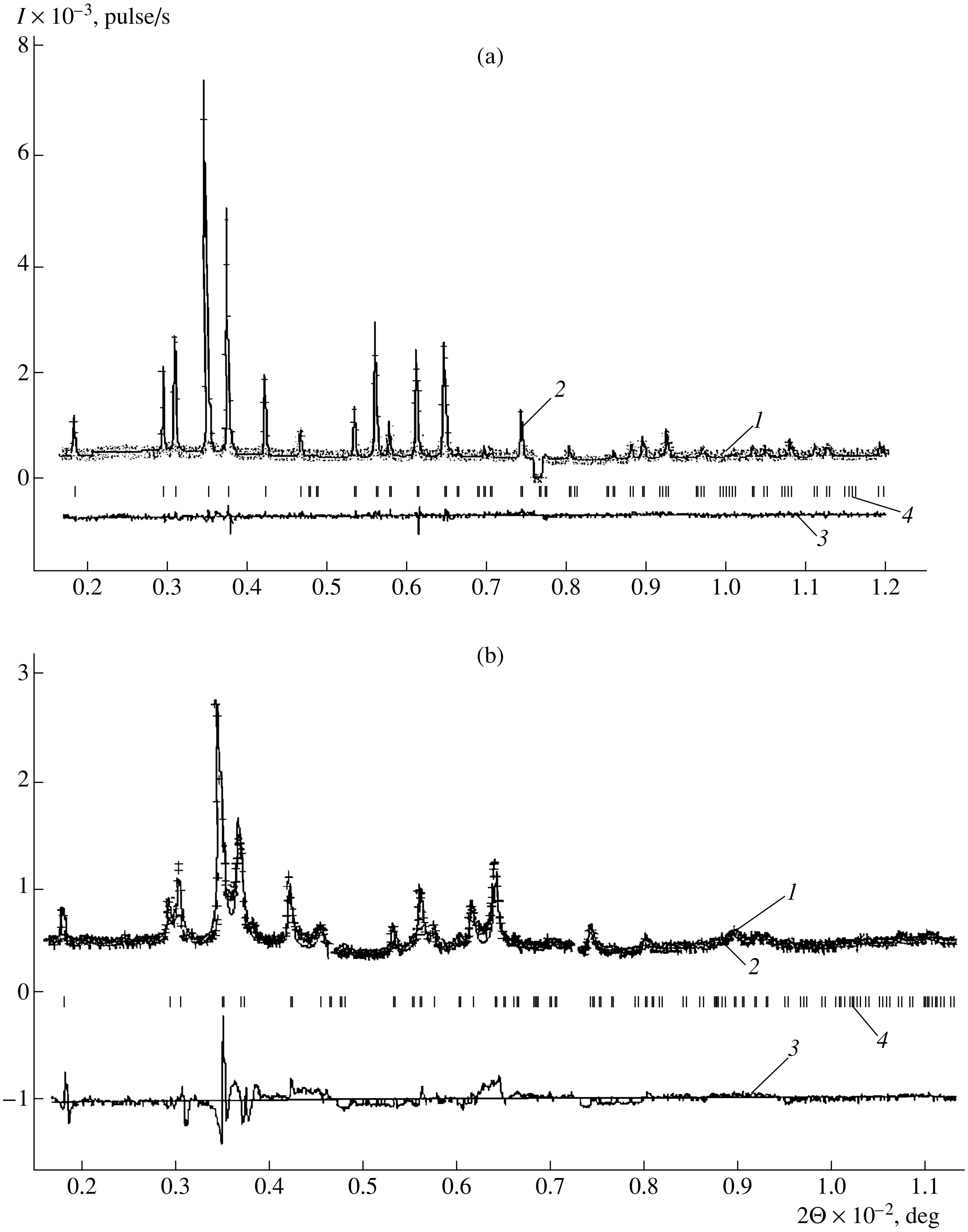

Fig. 2. (a) (*1*) Experimental (points) and (*2*) calculated according to the final model at $R = 0.05$ (lines) X-ray patterns for the initial $CuCr_2O_4$; (*3*) the difference curve; and (*4*) bar diagram. (b) (*1*) Experimental (points) and (*2*) calculated according to the final model at $R = 0.07$ (lines) X-ray patterns for reoxidized copper chromite; (*3*) the difference curve; and (*4*) bar diagram.

Comparison of the results obtained with data reported in [8] showed that there is no substantial difference between them. Some deviations in the lattice parameters and atomic coordinates are explainable by a difference in sample preparation procedures.

Let us consider the structure of reoxidized copper chromite. As we noted above, reoxidized chromite is formed by the oxidation of an epitaxially bound system of phases—metallic copper and cation-deficient cubic spinel stabilized by protons.

As we see from diffraction patterns (Fig. 1, curve *3*), reoxidized chromite has a structure of tetragonal-distorted spinel, but the parameters of spinel in the initial and reoxidized samples are somewhat different (see

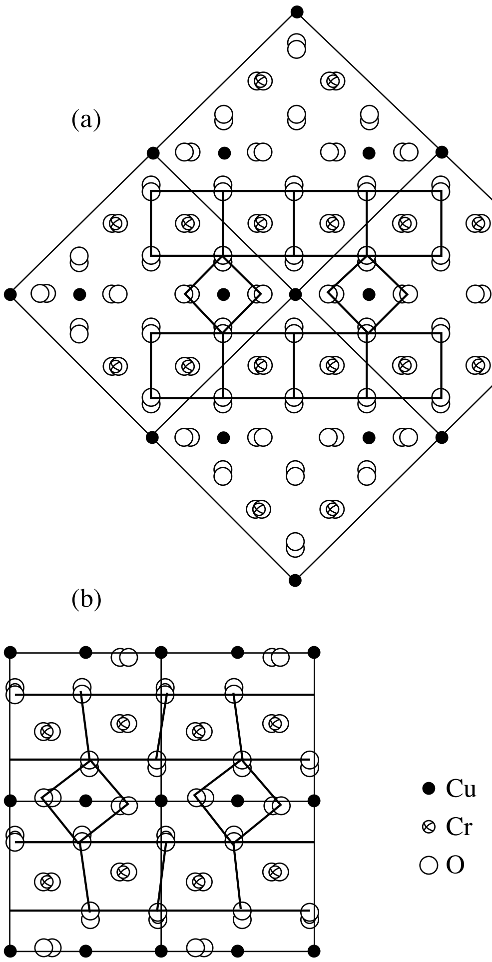

Fig. 3. Projection onto the (001) plane of (a) the cubic and (b) tetragonal-distorted structures of spinel.

Table 2). The ratio c/a in the reoxidized sample is 1.32, whereas it is 1.29 in the initial state.

Detailed comparison of the diffraction patterns of initial and reoxidized samples suggests the broadening of the diffraction lines in the case of the reoxidized sample (Fig. 2). Calculation of the regions of coherent scattering along the [111] direction shows that the reduction–reoxidation process leads to a change in the dispersity from ~1500 Å in the initial sample to ~500 Å in the reoxidized sample. This agrees with a difference in the surface areas in these samples.

Figure 2b shows the experimental and calculated diffraction patterns of reoxidized copper chromite. The latter was obtained using the final model of refinement. The refined structural parameters are shown in Table 2. As can be seen from Table 2 and Fig. 2, copper, chromium, and oxygen atoms in the initial sample are distributed in the crystallographic positions according to the space group I-42d, although specific values of chromium and oxygen ion coordinates and the interatomic distances Cu–O and Cr–O differ from those for the initial sample. The filling of copper-ion positions shows the most pronounced difference from the initial sample. As follows from Table 2, the coefficient of filling is 0.8 for the reoxidized sample, which agrees with the differential dissolution data (Cu/Cr = 0.4), although for the stoichiometric spinel it equals 1. Therefore, some quantity of protons remains in the reoxidized spinel. Its formula is $[Cu]_{0.8}[Cr]_2O_{3.6}OH_{0.4}$.

Comparison of the structural formulas of the reduced and reoxidized chromites points to the fact that copper ions return to their positions in the spinel structure and the amount of protons decreases. It is likely that spinel does not completely returns to its stoichiometry because of the irreversible decomposition of the copper chromite surface layer due to the hydrogen interaction with spinel-surface oxygen and water formation at the initial moment [3].

Note that the structural transformation of cubic spinel into tetragonal spinel during reduction–reoxidation is not a polymorphic transition because spinel stoichiometry changes. According to Talanov [10], the ordering of distortions in the structural polyhedra takes place for the structures containing sufficient amount of Jahn–Teller ions. This condition is fulfilled for the stoichiometric spinel $CuCr_2O_4$. During reduction by hydrogen, the amount of copper ions in the spinel structure decreases due to their transition to Cu^{1+} in the octahedral positions of spinel and their transition to Cu^0 on the surface of cation-deficient spinel. The amount of Cu^{2+} remaining in the structure becomes insufficient for

Table 2. Refined structures of initial and reduced–reoxidized copper chromite

Sample	R*	Space group	a, Å	c, Å	c/a	Atomic coordinates			Cu–O, Å	Cr–O, Å
						Cu	Cr	O		
$CuCr_2O_4$ initial	0.05	I-42d	6.03(2)	7.78(6)	1.29	$x = 0$	$x = 0.497(9)$	$x = 0.281(6)$	1.935(4)	1.925(2)
						$y = 0$	$y = 0.250$	$y = 0.015(5)$		2.008(2)
						$z = 0$	$z = 0.125$	$z = 0.118(6)$		2.082(2)
$CuCr_2O_4$ reoxidized	0.07	I-42d	5.99(6)	7.91(3)	1.32	$x = 0$	$x = 0.478(7)$	$x = 0.268(1)$	1.867(4)	1.909(2)
						$y = 0$	$y = 0.250$	$y = 0.011(6)$		2.046(2)
						$z = 0$	$z = 0.125$	$z = 0.117(9)$		2.145(2)

* R is the discrepancy factor.

the ordering of distortions in polyhedra. Therefore, the cubic structure of spinel is observed for the reduced sample at all temperatures. During reoxidation, the amount of Cu^{2+} ions increases, and the property of structural polymorphism is recovered.

CONCLUSION

This structural study of the initial, reduced, and reoxidized copper chromite under different conditions showed that structural transformations in the processes of oxidation–reduction of copper chromite are associated with reversible substitution of copper ions for hydrogen. However, this process cannot be completely reversible because reduction leads to the decomposition of the surface layers of spinel. The study of the catalytic properties of copper chromite in acetone hydrogenation to isopropanol [2] showed that copper chromite is highly active only in the region of reversible hydrogen adsorption.

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REFERENCES

1. Jalowiecki-Duhamel, L., Sene, A., Wrobel, G., and Grimblot, J., *Int. J. Hydrogen Energy*, 1993, vol. 18, no. 11, p. 925.
2. Makarova, O.V., Yur’eva, T.M., Plyasova, L.M., *et al.*, *Kinet. Katal.*, 1993, vol. 34, no. 4, p. 681.
3. Khasin, A.V., Simentsova, I.I., and Yurieva, T.M., *React. Kinet. Catal. Lett.*, 1994, vol. 52, no. 1, p.113.
4. Plyasova, L.M., Solov’eva, L.P., Kriger, T.A., *et al.*, *Kinet. Katal.*, 1996, vol. 37, no. 4, p. 622.
5. Plyasova, L.M., Solovieva, L.P., Krieger, T.A., and Yurieva, T.M., *J. Mol. Catal. A: Chem.*, 1996, vol. 105, no. 1, p. 61.
6. Malakhov, V.V. and Vlasov, A.A., *Kinet. Katal.*, 1995, vol. 36, no. 4, p. 503.
7. Solov’eva, L.P., Tsybulya, S.V., and Zabolotnyi, V.A., *Polikristall – sistema programm dlya strukturnykh raschetov* (Polikristall: A Program Package for Structural Calculations), Novosibirsk: Inst. of Catalysis, 1993.
8. Prince, E., *Acta Crystallogr.*, 1957, vol. 10, p. 554.
9. Ust’yantsev, V.M. and Mar’evich, V.I., *Izv. Akad. Nauk SSSR, Ser. Neorg. Mater.*, 1973, vol. 9, no. 2, p. 336.
10. Talanov, V.M., *Izv. Akad. Nauk SSSR, Ser. Neorg. Mater.*, 1989, vol. 25, no. 6, p.1001.