

Structure transformations of copper chromite under reduction–reoxidation conditions

L.M. Plyasova^{*}, I.Yu. Molina, T.A. Krieger, L.P. Davydova, T.M. Yurieva

Boreskov Institute of Catalysis SB RAS, Prospect Academica Lavrentieva 5, Novosibirsk 630090, Russia

Abstract

Structure transformations accompanying reoxidation preliminary reduced at 270°C copper chromite were studied using X-ray powder diffraction method, and comparison of the structures of the initial and reoxidized copper chromite was carried out. Conditions under which cation-deficient spinel, stabilized with hydrogen and epitaxially bonded with its surface Cu⁰ particles (derived from reduction of copper chromite by hydrogen) forms copper chromite with the tetragonal spinel structure are revealed. It is shown that the reoxidized spinel is non-stoichiometric and possibly contains some amount of hydrogen in the form of protons bonded to the lattice oxygen. Differences of reversible phase transformation of copper chromite under reduction–reoxidation conditions from reversible polymorphism of copper chromite with temperature variations are analyzed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: X-ray powder diffraction; Structure; Copper chromite; Hydrogen

1. Introduction

Using in situ X-ray powder diffraction, it was shown [1] that the interaction of hydrogen with copper chromite in the temperature range of 180–350°C does not cause the destruction transformation of the spinel. Investigation of the reduction process of copper chromite with the kinetic method [2] showed that only surface oxygen of copper chromite interacts with hydrogen-yielding water and fundamental reduction is not concerned with the destruction of the chromite. As shown by detailed structure inves-

tigation with X-ray and neutron powder diffraction [3,4], reduction of copper chromite at medium temperatures leads to oxidation–reduction replacement of Cu²⁺ ions in oxygen tetrahedrons of the spinel by protons with the formation of: (1) Cu⁰ particles epitaxially bonded with the surface of cation-deficient spinel and (2) Cu¹⁺ ions in oxygen octahedrons of the spinel. Furthermore, part of the occluded hydrogen is distributed in octahedral positions as neutral atoms and their presence are not concerned with valence transformation of copper. Under certain conditions of reoxidation, the resetting of Cu⁰ and Cu¹⁺ to Cu²⁺ valence state and the reconstruction of the spinel to the initial structure take place.

In the present paper, conditions of reversible transformations in copper chromite under reduc-

^{*} Corresponding author. Tel.: +7-3832-341300; fax: +7-3832-343056.

E-mail address: pls@catalysis.nsk.su (L.M. Plyasova).

tion–reoxidation conditions are revealed and the analysis of structure transformations accompanying this process is carried out. The structure of the reoxidized copper chromite is investigated: such a study is a necessary step to determine the mechanism of catalytical action of copper-containing oxide catalysts.

2. Experimental

The initial sample of copper chromite was prepared by thermal decomposition of copper chromium hydroxocarbonate in air following calcination at $T = 900^\circ\text{C}$ [1].

Treatment of the initial sample in various gas mediums was conducted in a quartz flow-type reactor. The reduction was carried out at $T = 270^\circ\text{C}$ for 3–4 h. Then the reduced sample was held for 3 h at $T \sim 290^\circ\text{C}$ either in helium purified from traces of oxygen or in non-purified helium containing 0.05 vol.% of O_2 . After each experiment, the sample was cooled up to room temperature and X-ray powder diffraction study of the sample was carried out.

To elucidate structural features of the reoxidized copper chromite, the structures of the initial and reoxidized samples were compared. The X-ray diffraction patterns were obtained using a URD-63 diffractometer (Germany) in $\text{CuK}\alpha$ -radiation with a scanning method within the angle interval $2\theta = 15\text{--}140^\circ$ (with 0.02° step) and the exposition time of 10–20 s. The GSAS program and a program system ‘‘Polikristall’’ [5] were used to treat the experimental data and to refine the structures.

3. Results and discussion

3.1. Phase composition of the initial, reduced and reoxidized samples

Diffraction patterns of the initial copper chromite (a), the reduced copper chromite (b),

copper chromite heated in helium containing ~ 0.05 vol.% O_2 (c), and helium purified from traces of oxygen (d) are presented in Fig. 1. From X-ray powder diffraction data, it follows that the initial sample is a tetragonally distorted spinel with impurity of $\alpha\text{-Cr}_2\text{O}_3$ (Fig. 1a). X-ray diffraction pattern of the reduced sample (Fig. 1b) is in agreement with that obtained under in situ reduction conditions which was analyzed in detail in literature [3,4]. The analysis showed that the reduced sample is a cubic spinel, the structure of which is stabilized with protons and according to X-ray and neutron powder diffraction data, has the structural formula $[\text{Cu}^{2+}]_{0.33-a}[\text{H}_{0.36}^+]_4[\text{Cu}_{0.07}^+]_2\text{Cr}_2\text{O}_4^e$, where a, c, d, and e are crystallographic positions of atoms in the spinel structure. The atomic ratio $\text{Cu}^{2+} + \text{Cu}^{1+}/\text{Cr}^{3+}$ is 0.235 whereas $\text{Cu}/\text{Cr} = 0.5$ for the initial sample. Therefore $\sim 50\%$ of copper ions turn into Cu^0 state. When treating the reduced sample with the inert gas purified from traces of oxygen for 20 h, the resetting of copper into the spinel structure does not occur (Fig. 1b,d). Change of the diffraction pattern takes place after treatment of the reduced sample with He

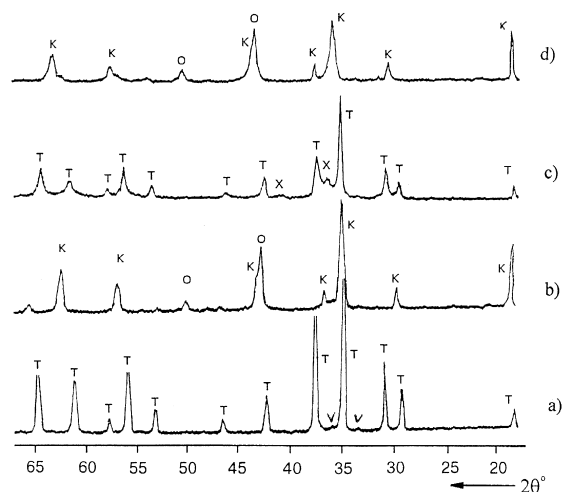


Fig. 1. X-ray diffraction patterns of copper chromite: (a) the initial sample, (b) the sample after treatment in hydrogen at 270°C , (c) sample after treatment in non-purified helium at 290°C , and (d) sample after treatment in purified helium at 290°C ; T — tetragonal spinel, K — cubic spinel, O — Cu^0 , X — Cu_2O , V — Cr_2O_3 .

containing impurity of oxygen (Fig. 1c): metallic copper phase disappears and the spinel structure again becomes tetragonally distorted at room temperature. Moreover, traces of copper oxide are observed.

After treatment of the reduced sample with air up to $T = 630^\circ\text{C}$, oxidation of the copper metal to Cu_2O and/or CuO takes place; cation-deficient spinel decomposes, forming CuCrO_2 and $\alpha\text{-Cr}_2\text{O}_3$.

From the given data, it is evident that oxidation of copper atoms to Cu^{2+} state and their return to the copper chromite structure with noticeable rate take place only in helium flow containing impurity of oxygen. Obviously, this process is concerned with interaction of protons that stabilize the cation-deficient spinel; but direct exchanging interaction $\text{Cu}^0 + 2\text{H}^+ = \text{Cu}^{2+} + \text{H}_2$ is hindered and transition of electrons from copper to protons is significantly promoted by intermediate interaction with oxygen by the reaction: $2\text{Cu}^0 + \text{O}_2 + 4\text{H}^+ = 2\text{Cu}^{2+} + 2\text{H}_2\text{O}$. Increase in oxygen concentration and temperature (reoxidation in air at $T = 630^\circ\text{C}$) causes the fast oxidation of metallic copper to copper oxide ($2\text{Cu}^0 + \text{O}_2 = 2\text{CuO}$); as a result, copper ions do not return to the spinel structure and cation-deficient spinel passes into CuCrO_2 .

3.2. Comparison of the structures of the initial and reoxidized copper chromite

Copper chromite structure was first investigated by Prince in 1957 with neutron powder

diffraction method [6]. In the present paper, the refinement of the structure of the initial copper chromite is carried out using X-ray powder diffraction data. Results of the refinement of the structure within the framework of $I-42d$ space group are listed in Table 1. Experimental and calculated data from the final model diffraction patterns are given on Fig. 2a. It could be seen that calculated and experimental data agree closely with each other. In accordance with the given space group for tetragonally distorted spinel, all tetrahedral positions (4a) are occupied with copper ions, octahedral (8d) with chromium ions, and (16e) with oxygen ions. Analysis of interatomic distances showed that Cu^{2+} ions are surrounded by four oxygen ions with identical distances $\text{Cu}-\text{O}$ equal to 1.935 \AA , forming distorted tetrahedron with corners $\sim 103^\circ$ that is slightly less than in a regular tetrahedron ($\sim 109^\circ$). It seems likely that in such a way, Cu^{2+} ions tend to occupy characteristic square-plane coordination and distortion of the polyhedron because of Jahn–Teller effect occurs. Tetrahedron deformation causes distortions of octahedrons and displacement of chromium ions. Ordered arrangement of distorted polyhedrons gives rise to the occurrence of tetragonally distorted spinel structure. When increasing temperature, thermal motion of atoms leads to the disordering of distortions in polyhedrons and the structure is described as statistically cubic. As known, tetragonally distorted copper chromite becomes cubic at $T = 560^\circ\text{C}$ [7]. Parameters of cubic and tetragonal unit cells are connected by the ratio $a = \sqrt{2} / 2 A$, $c = A$,

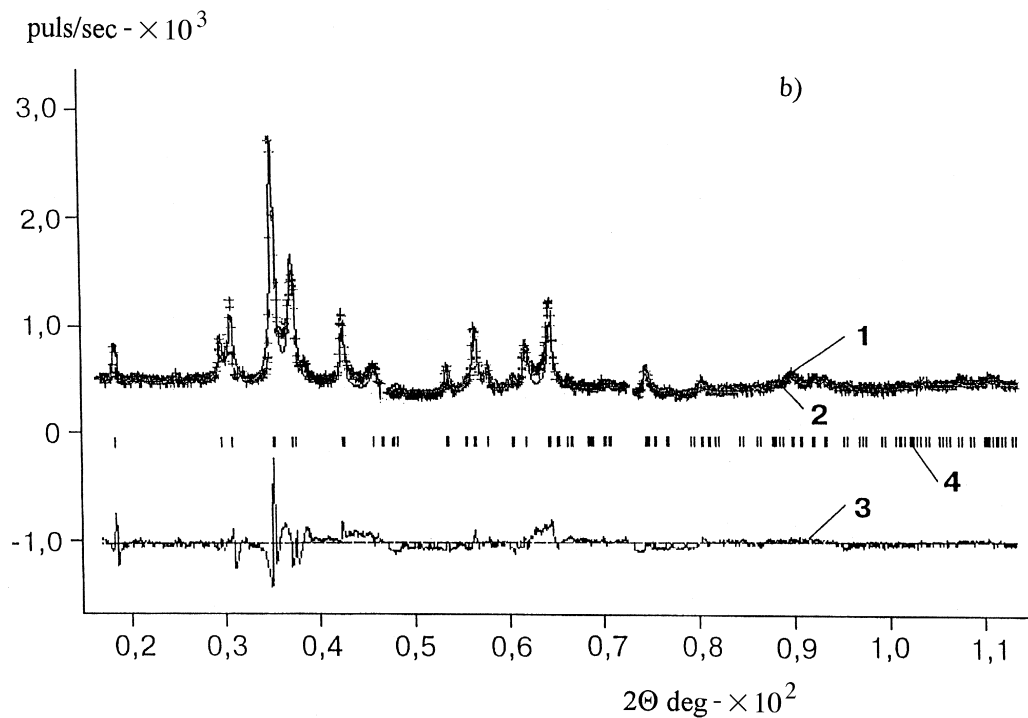
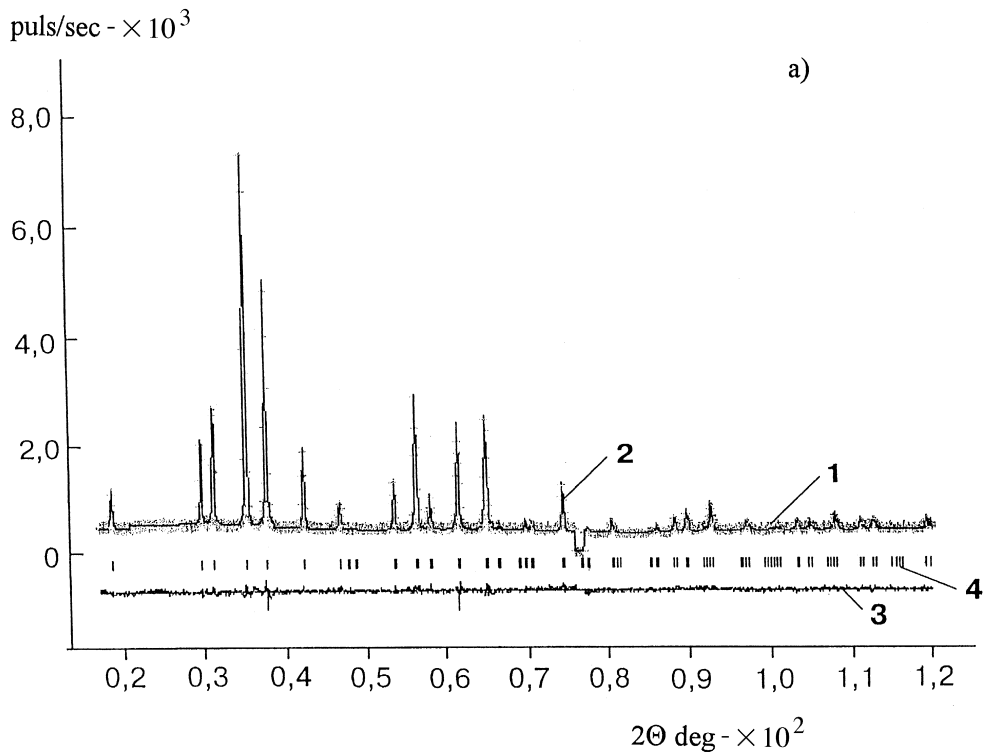
Table 1

Results of the refinement of the structures of the initial and reoxidized after reduction copper chromite

Sample	R	Space group	$a, \text{ \AA}$	$c, \text{ \AA}$	c/a	Cu (x, y, z)	Cr (x, y, z)	O (x, y, z)
CuCr_2O_4 , initial	0.05	$I-42d$	6.030	7.786	1.291	0,0,0 occupation degree = 1.0	0.4979, 0.250, 0.125	0.2816, 0.0155, 0.1186
CuCr_2O_4 , reoxidized	0.07	$I-42d$	5.996	7.913	1.319	0,0,0 occupation degree = 0.8	0.4787, 0.250, 0.125	0.2680, 0.0116, 0.1179

where A is the parameter of cubic unit cell and a , c are parameters of the tetragonal unit cell.

As it was shown [8], tetragonal \rightleftharpoons cubic transformation of CuCr_2O_4 occurs by the shift of



oxygen and chromium ions in tetragonally distorted unit cell from their equilibrium positions in cubic unit cell.

Let us discuss the structure of the reoxidized copper chromite. As it was noted, the reoxidized copper chromite is formed by the oxidation of epitaxially bonded system of phases — metallic copper and cation-deficient cubic spinel stabilized with hydrogen. As it can be seen from the given data (Fig. 1c), the reoxidized copper chromite also has the structure of tetragonally distorted spinel; however, the initial and reoxidized samples slightly differ in unit cell parameters (Table 1). The broadening of the diffraction lines of the reoxidized sample could be seen when comparing diffraction patterns in detail (Fig. 2a,b). Calculation of regions of coherent scattering in [111] direction indicates that under reduction–reoxidation conditions, dispersion varies from ~ 1500 Å for the initial sample to ~ 500 Å for the reoxidized sample that agrees with the changes in values of surface areas of this samples. Experimental and calculated from the final model of the refinement, diffraction patterns are shown in Fig. 2b. Results of the refinement of the structural parameters are given in Table 1. As well as for the initial sample copper, chromium and oxygen ions are located in crystallographic positions within the framework of $I-42d$ space group, though values of coordinates of chromium and oxygen ions and Cu–O and Cr–O interatomic distances differ from that of the initial sample. But the main difference between the initial and reoxidized samples is the value of occupation degree of (4a) positions by copper ions. As one can see from the table, this coefficient is 0.8 for the reoxidized sample whereas for the stoichiometric spinel, it is equal to 1. It follows that probably some amount of protons remain in the reoxi-

dized spinel and its formula can be written as $[\text{Cu}^{2+}]_{0.8}^a[\text{H}_{0.1}^+]_4^c[\text{Cr}]_2^d\text{O}_4^e$. Comparison of structural formulae of the reduced and reoxidized copper chromite indicates that copper ions return to their positions in the spinel structure and the amount of protons decrease. Apparently, full restitution to the spinel stoichiometry does not occur because of nonreversible destruction of the surface layer of copper chromite as a result of interaction of hydrogen with the spinel surface oxygen with formation of water [2].

4. Conclusions

Hence, investigation of the structures of the initial, reduced [4], and reoxidized copper chromite under various conditions showed that structural transformations under reduction–reoxidation conditions are dealt with reversible substitution of copper ions on hydrogen. However, this process could not be completely reversible as destruction of the spinel surface layers occurs under reduction conditions.

Tetragonal-to-cubic structural transformation of the spinel under reduction–reoxidation conditions could not be considered as polymorphous transformation, because as a result of this phase transformation, the stoichiometric composition of the spinel changes. According to Ref. [8], ordering of the distortions in polyhedrons occurs for the structures that contain sufficient amount of Jahn–Teller ions. This condition is obeyed for the stoichiometric spinel. Under reduction conditions, the amount of Cu^{2+} ions in the spinel structure is reduced as a consequence of their transition to Cu^+ state in octahedral positions of the spinel (1) and to Cu^0 state on the surface of cation-deficient spinel (2) and the

Fig. 2. (a) Experimental (1) and calculated (2) data from the final model with uncertainty factor $R = 0.05$ diffraction patterns for the initial CuCr_2O_4 ; difference curve (3), theoretical calculation of interplane distances (4). (b) Experimental (1) and calculated (2) data from the final model with uncertainty factor $R = 0.07$ diffraction patterns for the reoxidized CuCr_2O_4 ; difference curve (3), theoretical calculation of interplane distances (4).

remaining structure amount of Cu^{2+} ions is not enough for ordering the distortions in polyhedrons. Therefore, statistically cubic spinel structure is observed for the reduced sample at all temperatures. Under reoxidation conditions, the amount of Cu^{2+} ions in the spinel structure increases and the property of high-temperature polymorphism reverts to the spinel.

Acknowledgements

The work was made under financial support of NWO-047.005.03.96 grant.

References

- [1] O.V. Makarova, T.M. Yurieva, G.N. Kustova, A.V. Ziborov, L.M. Plyasova, T.P. Minukova, V.I. Zaikoushii, *Kinet. Catal.* 34 (4) (1993) 608, (in English).
- [2] A.V. Khasin, I.I. Simentsova, T.M. Yurieva, *React. Kinet. Catal. Lett.* 52 (1) (1994) 113.
- [3] L.M. Plyasova, L.P. Solov'eva, T.A. Krieger, O.V. Makarova, T.M. Yurieva, *Kinet. Catal.* 37 (4) (1996) 622, (in English).
- [4] L.M. Plyasova, T.A. Krieger, O.V. Makarova, T.M. Yurieva, *J. Mol. Catal. A: Chem.* 105 (1996) 61.
- [5] L.P. Solov'eva, S.V. Tsybulya, V.A. Zabolotnyi, *Polikristall — A Program System for Structural Calculations*, Institute of Catalysis, Novosibirsk, 1993, (in Russian).
- [6] E. Prince, *Acta Crystallogr.* 10 (1957) 554.
- [7] V.M. Ust'yantsev, V.I. Mar'evich, *Neorg. Mater.* 9 (2) (1973) 336, (in Russian).
- [8] V.M. Talanov, *Neorg. Mater.* 25 (6) (1989) 1001, (in Russian).