

# The nature of hydrogen stabilization in the reduced copper chromites

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## Abstract

In situ powder X-ray and neutron diffraction showed that copper chromite retains its spinel structure (space group  $Fd\bar{3}m$ ,  $a = 8.348(3) \text{ \AA}$ ) in hydrogen at 320°C. The spinel has a copper ion deficiency and is stabilized by the dissolved hydrogen. Two hydrogen states are observed in the spinel structure: as specific hydrogen species H (16c interstitial position) and as OH groups with covalent bonding (32e crystallographic position). The hydrogen species bonded to the lattice oxygen is formed as a result of the exchange interaction between hydrogen atoms and  $\text{Cu}^{2+}$  ions. In this case a portion of copper ions are reduced to  $\text{Cu}^0$  as flat particles onto the surface; another portion is reduced to  $\text{Cu}^{1+}$  and transferred towards the 16c positions.

*Keywords:* Powder X-ray diffraction; Neutron diffraction; Structure; Copper; Chromite; Hydrogen

## 1. Introduction

The goal of this work was the investigation of specific features of the reduced chromite structure, the dissolved hydrogen stabilization sites in the structure of the reduced chromite using X-ray and neutron diffraction. This state of catalyst became of great interest owing to the high catalytic activity of copper chromite for hydrogenation [1,2].

## 2. Experimental

Copper chromite  $\text{CuCr}_2\text{O}_4$  was the material of our studies. The preparation procedure of the material and its structural properties were discussed elsewhere [1]. The reduction of copper chromite was conducted at 320°C in hydrogen for 2 h.

X-ray studies in  $\text{CuK}_\alpha$  radiation (a reflected-beam graphite monochromator) were carried out using a diffractometer D-500 produced by Siemens. In situ experiments were conducted in a X-ray chamber reactor [3] linked to a controllable gas-supplying system. In order to avoid the influence of temperature on the diffraction peak intensities, the sample was

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brought down to room temperature. Scanning was conducted within the  $2\theta$  angle interval  $20\text{--}90^\circ$  with  $0.05^\circ$  step, the background fluctuations were below 3% during the measurement time.

Neutron diffraction of the samples were performed at the Berlin Neutron Scattering Centre, Germany. The sample to be studied was prepared by passing a hydrogen flow through a copper chromite-containing reactor at  $320^\circ\text{C}$ , then it was sealed in a quartz ampoule out of contact with air. Scanning was conducted within the  $2\theta$  angle interval  $8\text{--}80^\circ$  with  $0.1^\circ$  step,  $\lambda = 1.21 \text{ \AA}$ .

The obtained X-ray and neutronographic experimental data were processed with the help of the program package POLIKRISTALL [4] adapted for IBM/PC.

The structure of the cation-deficient spinel saturated with hydrogen was refined using integral intensity of the peaks. In the case of superposition of peaks corresponding to copper chromite and copper metal, the contribution of

the latter was subtracted from the total integral intensity [5].

### 3. Results and discussion

X-ray patterns recorded for the initial copper chromite and for the sample after their exposition to the hydrogen flow at  $320^\circ\text{C}$  during 2 h are shown in Fig. 1. In the patterns of the reduced samples the lines corresponding to copper metal and cubic spinel are seen (the initial sample possesses the structure of the tetragonally spinel [6]). XRD data show 42 at.% copper chromite reduced to  $\text{Cu}^0$ .

The calculations show that for the cubic chromite there is an essential difference between experimental patterns and calculated one. The removal of ca. 50% copper from the lattice results in much more similarity between them (the uncertainty factor  $R = 0.08$ ). A further decrease in the  $R$  factor was achieved with the model in which part of the rest copper ions were

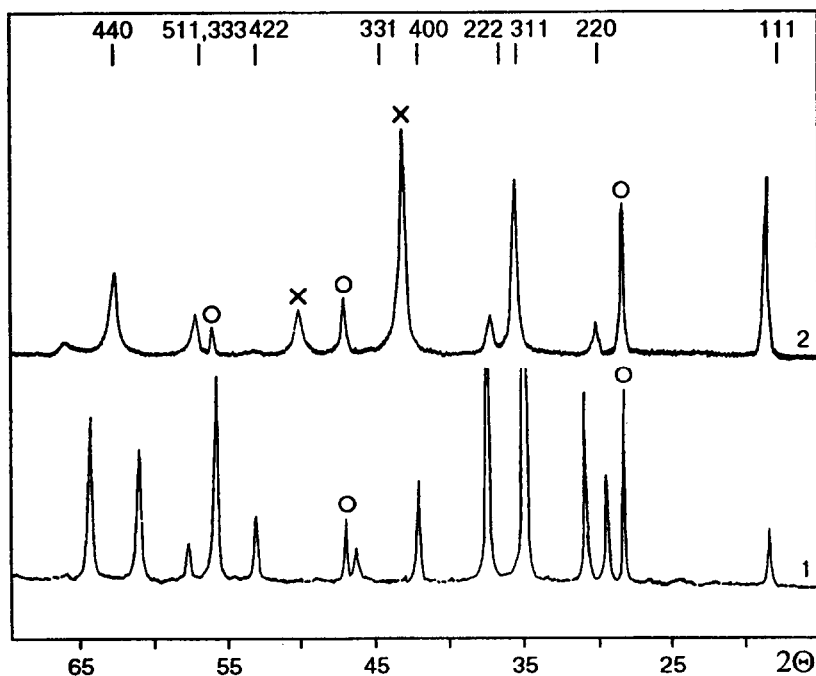


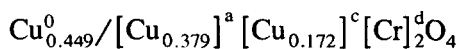
Fig. 1. X-ray patterns of copper chromite: 1 – the starting sample; 2 – the sample after 2 h in hydrogen at  $320^\circ\text{C}$ , (x)  $\text{Cu}^0$ , (o) Si standard, the remaining peaks:  $\text{CuCr}_2\text{O}_4$ .

Table 1

Coordinates, isotropic parameters of atoms, position occupations for the model of reduced copper chromite (from X-ray diffraction)

Atom	Position	Occupation	x	y	z	B(isot)
Cu <sub>1</sub>	8a	0.379	0.125	0.125	0.125	2.07
Cu <sub>2</sub>	16c	0.086	0	0	0	1.3
Cr	16d	1	0.5	0.5	0.5	0.24
O	32e	1	0.254	0.254	0.254	1.75

moved from 8a to 16c. None of other possible positions was found to lower the *R* factor. The cationic coordinates and isotropic atomic parameters for model with *R* = 0.038 are summarized in Table 1. The refinement was made implying the space group *Fd3m*, *a* = 8.348(3) Å. The experimental and calculated X-ray patterns are shown in Fig. 2. Phase composition of the sample corresponds to the formula:



where [ ]<sup>a, c, d</sup> are the crystallographic positions of the ions in the spinel structure.

Apparently, protons compensate the stoichiometry violation in the spinel. The dissolved hydrogen species and their arrangement in the reduced chromite structure were identified using the neutron diagrams. *R* factor equal to 0.42 for the neutron diagram was calculated according to the model developed from the XRD data without considering the dissolved hydrogen.

A significant lowering of *R* factor (*R* = 0.093) was found for only two of the hydrogen positions: position 32e – tetrahedrons whose centers were occupied by copper ions before the reduction, and position 16c – centers of the empty octahedrons. Table 2 presents the coordinates of hydrogen atoms, the occupation degree of the crystallographic positions, and isotropic heat parameters (*R* = 0.056). The correlation between the experimental neutron diagram and

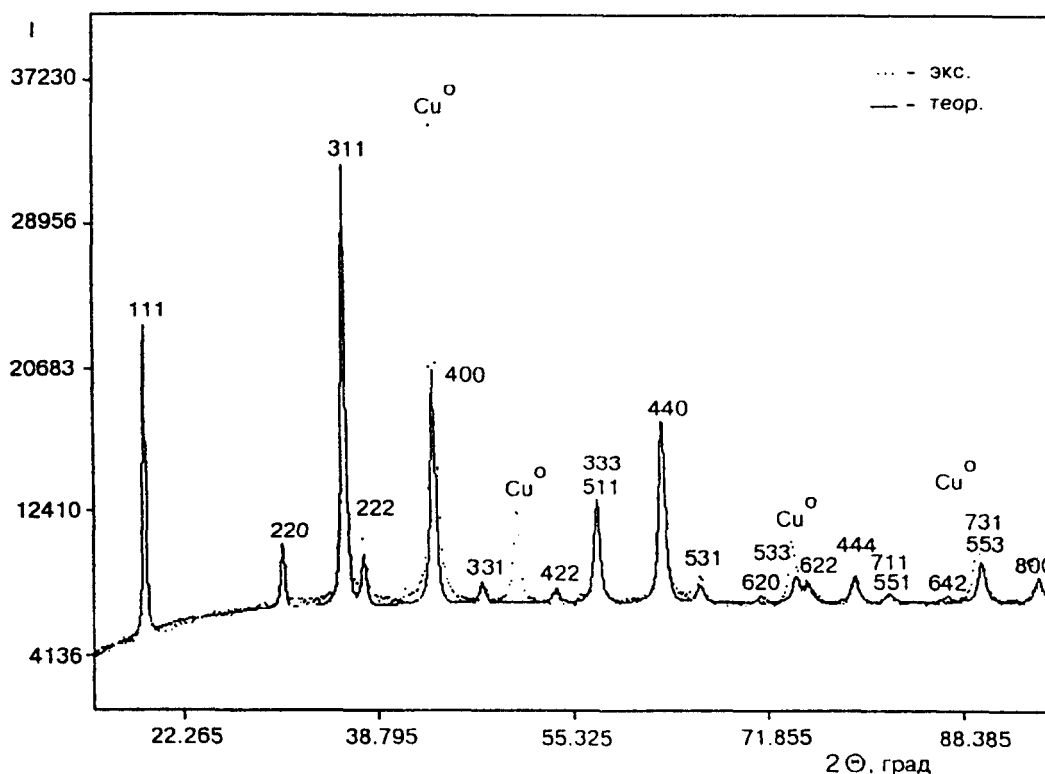


Fig. 2. Experimental X-ray diffraction pattern of the reduced copper chromite and the pattern calculated for the suggested model. (···) experimental, (—) theoretical.  $\theta$  in degrees.

Table 2

Coordinates, isotropic parameters of atoms, position occupations for the model of reduced copper chromite (from neutron diffraction)

Atom	Position	Occupation	x	y	z	B(isot)
Cu <sub>1</sub>	8a	0.322	0.125	0.125	0.125	1.49
Cu <sub>2</sub>	16c	0.073	0	0	0	1
Cr	16d	1	0.5	0.5	0.5	0.23
O	32e	1	0.255	0.255	0.255	1.74
H <sub>1</sub>	32e	0.310	0.187	0.187	0.187	1.03
H <sub>2</sub>	16c	0.379	0	0	0	0.70

the pattern calculated using this model is shown in Table 3.

Some difference in the number of copper atoms in various positions, found from X-ray diffractograms and neutronograms, can be attributed to some difference in the degree of reduction of the samples in the camera reactor and in chemical reactor. But this difference is not principal. In what follows we discuss the neutron diffraction analysis data.

As seen from analysis of interatomic distances, the hydrogen at 32e position ( $x = 0.1875$ ) is shifted from the tetrahedron center towards its apex so that one O...H distance

Table 3

The experimental and the theoretical neutronodiagrams for the reduced copper chromite

hkl	2 $\theta$ , deg	I (exp)	I (theor.)	2 $\theta$ , deg
111	14.44	31	32	14.44
220	23.68	2	0	23.68
311	27.86	12	14	27.84
222	29.11	45	46	29.11
400	33.74	80	81	33.74
331	36.87	2	0	36.87
422		0	2	41.63
511 } 333 }	44.29	26	29 } 0 }	44.29
440	48.45	100	102	48.46
531	50.83	10	9	50.83
442	51.60	2	2	51.60
620	54.62	5	3	54.62
533	56.81	12	13	56.81
622	57.53	34	35	57.53
444	60.34	28	28	60.34
711 } 551 }	62.40	7	0 } 5 }	62.41
642	65.76	4	2	65.76

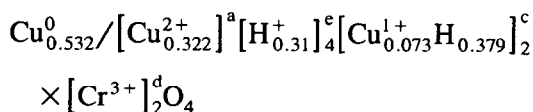
equals 0.96 Å, and the other three equal 2.33 Å. The distance 0.96 Å argues in favor of the formation of a covalent bond O...H, like in a water molecule [7]. The chemical interaction indicates that prior to the interaction the hydrogen in a tetrahedron resembles a proton.

The hydrogen at 16c is at the same distances 2.12 Å from all six oxygen atoms. The coordination and the value of O–H distance indicate that this hydrogen cannot be considered as the well-known species of such types as OH<sup>-</sup>, H<sub>3</sub>O<sup>+</sup>, H<sub>2</sub>O, etc. [7,11–13]. It is probably a mobile uncharged species H. A similar state of hydrogen has been suggested by other authors [10].

The cation distribution in the copper chromite reduced under the conditions of neutron diffraction experiments (see Table 2) shows that in the formula unit 0.322 Cu<sup>2+</sup> ions are held unchanged in their tetrahedral positions, 0.532 copper ions are reduced to Cu<sup>0</sup> and move onto the spinel crystal surface, and 0.146 copper ions (probably Cu<sup>1+</sup>) transfer to the 16c positions. Cr<sup>3+</sup> ions are held unchanged in the 16d positions.

We assume that hydrogen atoms generated at the partially reduced chromite surface [8] penetrate into the spinel structure. There are possible two types of dissolved hydrogen interaction with copper ions in the tetrahedrons. Two hydrogen atoms react with a copper ion to form a copper atom which is released on the chromite surface and two hydroxyl species. Single hydrogen atom reduces a copper ion to Cu<sup>1+</sup> and forms one hydroxyl group in the structure, the Cu<sup>1+</sup> ion transfers to 16c. The occurrence of Cu<sup>+</sup> ions in the reduced chromite was reported in [9,10].

Taking into account the Cu<sup>0</sup> atoms released at the chromite surface and the dissolved hydrogen, the reduced copper chromite can be presented as follows:



The data obtained allow the conclusion that

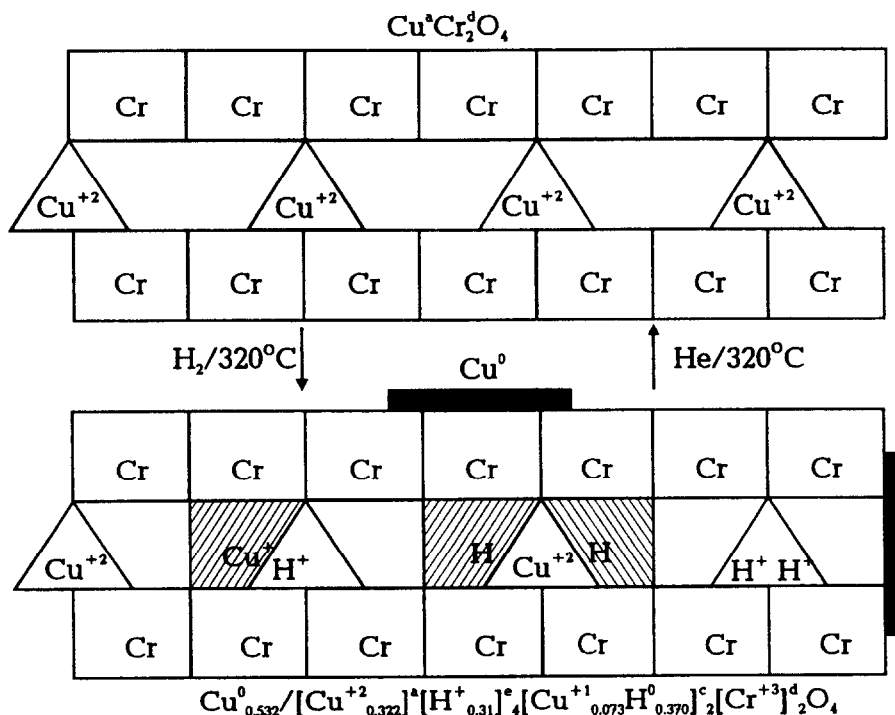


Fig. 3. The scheme of the reversible reduction of copper chromite. Triangles indicate (a) tetrahedral positions; squares indicate (d) octahedral positions; hatched areas indicate (c) octahedral positions.

hydrogen is dissolved indeed in the reduced chromite. There are two states of the dissolved hydrogen: (1) the unusual hydrogen atomic species inserted into the spinel interstices; and (2) protons at tetrahedrons, which form the covalent bond  $\text{O} \cdots \text{H}$  with the lattice oxygen.

Even if the concentration and the cation distribution in the reduced chromite differ essentially from those in the stoichiometric spinel, its structure is held due to occupation the tetrahedrons by protons and stability in  $\text{Cr}^{3+}$  positions. This is why the chromite can regain its initial state with the structure of the stoichiometric spinel upon removal of the hydrogen.

The reduction process of copper chromite is represented schematically in Fig. 3.

Authors of Ref. [10] using different physicochemical (but non-structural) methods proposed the formula units of the reduced Cu–Cr catalysts including hydrogen as  $\text{OH}^-$  groups and  $\text{H}^*$ ; the latter seems likely to be uncharged

hydrogen species. Our data obtained by methods of structural analysis for well-crystallized samples of the stoichiometric composition support the conclusions of the previous study [10] and also enable the determination of the sites of localisation of  $\text{H}^+$  and  $\text{H}$  ( $\text{H}^*$  in terms of Ref. [10]) in the bulk of the reduced chromite. This is of great importance for understanding the mechanism of the catalyst activation and performance.

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## References

- [1] O.V. Makarova, T.M. Yurieva, G.N. Kustova, A.V. Ziborov, L.M. Plyasova, T.P. Minyukova, L.P. Davydova and V.I. Zaikovskii, *Kinet.Catal.*, **34** (1993) 608 (in English).
- [2] O.V. Makarova, T.M. Yurieva, L.M. Plyasova, T.A. Kriger and V.I. Zaikovskii, *Kinet. Catal.*, **35** (1994) 371 (in English).
- [3] A.L. Vishnevskii, V.V. Molchanov, T.A. Kriger and L.M. Plyasova, *Abstr. International Conference on Powder Diffraction and Crystal Chemistry, St.-Petersburg, 1994*, p. 208.
- [4] L.P. Solov'eva, S.V. Tsybulya and V.A. Zabolotnyi, *PO-LIKRISTALL – a program system for structural calculations, Novosibirsk, Institute of Catalysis, 1993* (in Russian).
- [5] F.M. Chung, *J. Appl. Crystallogr.*, **7** (1974) 519.
- [6] X-Ray Powder Data File JPDS, Philadelphia, PA, 1967, No. 26-509.
- [7] A.J. Gordon and R.A. Ford, *The Chemist's Companion. A Handbook of Practical Data, Techniques and References*. Moscow, Mir, 1976, p. 127 (translated into Russian).
- [8] A.V. Khasin, I.I. Simentsova and T.M. Yurieva, *React. Kinet. Catal. Lett.* **52** (1994) 113.
- [9] E.N. Yurchenko, A.I. Boronin, A.V. Ziborov, O.G. Korol'kova, N.G. Zubritskaya, and L.M. Plyasova, *Kinet. Katal.*, **33** (1992) 401 (in Russian).
- [10] G. Wrobel, A. d'Huysser and J.-P. Bonnelle, *Nouv. J. Chem.*, **8** (1984) 291.
- [11] Yu.Z. Nozic, R.P. Ozerov, K. Hennig, *Strukturная Neitronografiya, M., Atomizdat, 1979*, p. 319 (in Russian).
- [12] V. Luzzati, *Acta Crystallogr.*, **6** (1953) 157.
- [13] Y.K. Yoon, G.B. Carpenter, *Acta Crystallogr.*, **12** (1958) 17.