

Review

Mechanisms for hydrogenation of acetone to isopropanol and of carbon oxides to methanol over copper-containing oxide catalysts

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Abstract

Mechanisms for the synthesis of methanol from CO and CO₂ and for the hydrogenation of acetone to isopropanol are discussed based on the recent experimental results obtained by the authors. The state of copper-containing compounds in a hydrogen medium at 200–400°C and the nature of their interaction with the reaction components were studied. Hydrogenation of carbon oxides and acetone was proposed to be the result of the ability of copper ions to reversible transformations to generate copper metal and protons. Activation of acetone and CO₂ can be achieved through their interaction with Cu⁰, and activation of CO through its interaction with oxygen-containing sites of Cu⁺¹–O–Cu⁺¹ type which are formed after oxidation of a portion of Cu⁰ with carbon dioxide.

Keywords: Copper-containing oxide catalysts; Hydrogenation of acetone to isopropanol; Methanol synthesis from carbon oxides

1. Introduction

Copper-containing oxide catalysts are active for hydrogenation reactions, including hydrogenation of carbonyl groups of organic compounds and carbon oxides to alcohols. The aim of this paper is to discuss mechanisms of hydrogenation of acetone to isopropanol and of methanol synthesis from CO and CO₂. The considerations are based on analysis of recent experimental data on the effect of reaction medium components on the structure and the composition of the catalyst [1–7].

2. Experimental

Compounds of two types were chosen for the investigations:

(a) Copper chromite (CuCr₂O₄) is a component of numerous catalysts for hydrogenation of carbonyl bonds of organic compounds. The structure of this oxide is well known and convenient for experiments.

To prepare a sample of copper chromite, the complex hydroxide was coprecipitated from a solution of corresponding nitrates under the action of an ammonia solution and thermally decomposed at 900°C. XRD examination showed the sample to be a practically pure compound with the structure of tetragonally distorted spinel [8].

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Catalytic behavior of the chromite for hydrogenation of acetone to isopropyl alcohol was studied using a pulse flow installation with a fluidized catalyst bed. The reaction products were analyzed chromatographically.

(b) Solid solutions of copper ions in anion-modified (a-m) zinc oxide of the composition of $\text{Cu}_{0.08}\text{Zn}_{0.92}\text{O}^*$ and in a-m aluminium-containing zinc oxide of the composition $\text{Cu}_{0.15}\text{Zn}_{0.75}\text{Al}_{0.1}\text{O}^*{}^1$.

To prepare the samples, complex hydroxocarbonates of aurichalcite structure were coprecipitated by sodium hydrocarbonate from a mixture of solutions of corresponding nitrates, thoroughly washed, and decomposed at 350°C.

The catalytic behavior of the solid solution was studied in methanol synthesis at 220°C and atmospheric pressure [9]. The solid solution of copper ions in a-m ZnO of the above-mentioned composition was chosen as a model of copper–zinc–aluminium catalysts for methanol synthesis. Such a choice was made due to the fact that the rate of methanol synthesis is in proportion to the concentration of copper in solid solutions and reaches the values of the rates provided by the most active catalysts when the copper concentration is more than 30 at%.

3. Results and discussion

3.1. Nature of interaction between the catalysts and hydrogen

Typically, hydrogenation catalysts are activated by hydrogen before being used. That was why we studied first the composition and structure of the catalysts in their reduced states. In situ XRD, neutronographic, IR spectroscopic and electron microscopic techniques were used

for the studies, according to the procedures already described [1–5].

3.1.1. Structure of reduced copper chromite

A body of the results reported in [1,10,11] show that not only the running but also the starting temperature of the catalyst bed reduction determines the nature of the interaction of hydrogen and the copper chromite:

(1) If a sample of copper chromite is kept in air at up to 500°C and then reduced at higher temperatures, the chromite of Cu^+ of the delafossite structure is formed [10].

(2) Keeping a sample of copper chromite in flowing hydrogen at a starting temperature below 350–400°C and then at elevated temperatures to above 450°C results in the decomposition of the chromite to produce copper metal and chromia [1,11].

(3) Complex processes discussed below are observed with hydrogen flow passed through the chromite bed at 200–400°C [1].

Fig. 1a shows the electron microscopic image of the initial sample of CuCr_2O_4 . Copper ions are partially (50–60% from total copper content) reduced with hydrogen to Cu^0 and released as flat particles upon the surface of spinel crystals (Fig. 1c). These are well faceted particles of $50 \times 100 \times 100 \text{ \AA}$ in size which are bonded epitaxially to the spinel surface: compatibility between reciprocal lattice (111) planes of spinel and (111) planes of Cu^0 is seen from the superposition of spots (220) of copper and (440) of the chromite in the electron diffraction patterns (Fig. 1c). Such a state is destructed when the temperature is elevated to above 450°C; in this case the amount of released copper reaches almost 100%, Cu^0 particles become round shaped and only weakly bonded to the surface (Fig. 1b). The same state of catalyst is observed when reduced at a temperature lower than 320°C with H_2 catalyst, oxidized by O_2 at the same temperature and then treated with H_2 (Fig. 1b).

A spinel phase is preserved in flowing hydrogen at temperatures as high as 400°C. It is transformed to chromia upon complete release

¹ Anion-modified oxide containing OH^- and CO_3^{2-} -groups of precursors.

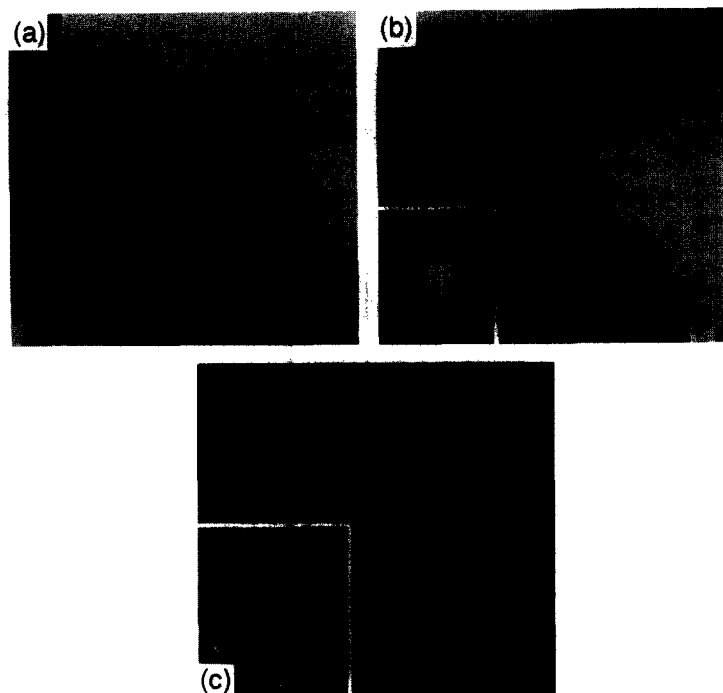


Fig. 1. Electron microscopic images ($\times 400000$) of the samples: initial CuCr_2O_4 (a); reduced in H_2 at 450°C (b); and reduced in H_2 at 320°C , the dark-field image of Cu^0 particles with identical orientation (c).

of copper at 450°C ; at first the structure of the NaCl type (Fig. 2a, curve 5) is formed, and then $\alpha\text{-Cr}_2\text{O}_3$. However, spinel acquires the cubic lattice with the lattice constant $a = 8.342 \text{ \AA}$

even at 250°C in hydrogen. The diffraction pattern recorded for it (Fig. 2a, curve 2) is characterized by the line intensity distribution which is rather different from that of the chromite untreated with H_2 (Fig. 2a, curve 1). When the temperature increases to 320°C , the difference of the line intensity distributions becomes even more apparent (Fig. 2a, curve 3). Note that the tetragonal distortion disappears at temperatures as high as 580°C in air [12].

The reduction at 250°C is seen from the IR spectroscopic data (Fig. 2b) to result in a decrease of the intensity of the absorption bands (a.b.) at 125 cm^{-1} and 193 cm^{-1} assigned to oscillations of the CuO_4 group of spinel (Fig. 2b, curves 1, 2) which are practically disappeared upon reduction at 320°C (Fig. 2b, curve 3). These data allow the conclusion that the amount of copper ions occupying tetrahedral positions depends on the reduction temperature: it decreases with elevation of temperature and practically disappears when the reduction is conducted at 320°C . It should be pointed out

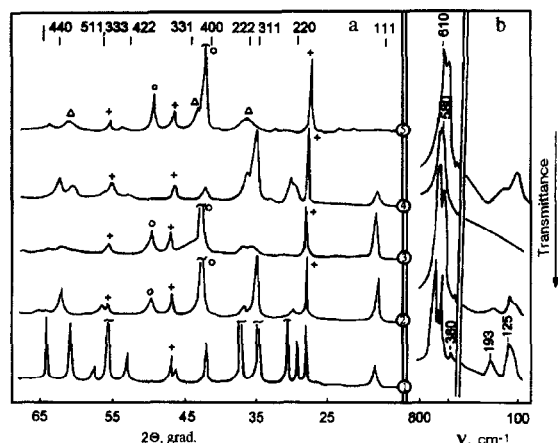


Fig. 2. X-ray diffraction patterns (a) and IR spectra (b) of copper chromite: 1 – initial sample; 2, 3, 5 – reduced in H_2 at 250° , 320° and 450°C , respectively; 4 – sample 3 calcined in He at 320°C for 10 h; (O), (+), (Δ) – reflections from the Cu^0 , silicon and NaCl-type structure, respectively. Positions of the reflections from a cubic type of CuCr_2O_4 spinel are marked on the top.

with the reference to the XRD data, that only a half of the copper ions are released as metallic particles under these conditions. The occurrence of another half of copper ions will be discussed later.

When the kinetic method [13] was used to study the interaction of hydrogen and the copper chromite at 220–350°C, only a portion of the reacting hydrogen which corresponds to approximately a half of the oxygen monolayer at the chromite surface was found to yield water, the rest of hydrogen is absorbed by the spinel.

The composition of the reduced chromite undergoes considerable transformations under the action of inert atmosphere, how it is seen from the in situ XRD (Fig. 2a, curve 4) and ex situ IR (Fig. 2b, curve 4) spectroscopic data. The following was observed upon substitution of flowing helium for flowing hydrogen (the sample was kept in helium for 10 h):

– in the diffraction pattern, the spots assigned to copper metal decrease and become practically unobservable; the spinel line intensity distribution varies towards that of the initial oxidized spinel;

– in the IR spectra, a.b.s. assigned to tetrahedral CuO_4 groups appear and attain their initial intensity.

Hence, the initial oxidized structure of the sample is restored in flowing helium. A repeated reduction in flowing hydrogen results in a full reproduction of the sample structure described above. The only explanation for the reversible transformations of the chromite upon medium variations ($\text{H}_2 \rightarrow \text{He} \rightarrow \text{H}_2$) may be that the interaction of hydrogen and the sample generates protons which are then reduced in flowing helium to form hydrogen to be desorbed. When we take into account the phase composition of the sample in various media, it seems unambiguous that the following processes occur:

1. $\text{H}_2 \rightleftharpoons 2\text{H}$;
2. $2\text{H} + \text{Cu}^{+2} \rightleftharpoons 2\text{H}^+ + \text{Cu}^0$.

In situ XRD technique was used to study the sample composition depending on the time of

Table 1
Experimental and calculated diffraction patterns for various models of copper chromite

hkl	$I_1(\text{exp})$	$I_2(\text{exp})$	I calculated according to model			
			I	II	III	IV
111	48	65	2	35	65	54
220	13	0	36	15	6	0
311	100	56	100	100	82	23
222	25	21	6	10	29	32
400	77	100	14	42	100	100
331	4	0	0	5	9	8
422	3	0	12	5	2	0
333	31	0	6	6	5	1
511			24	25	22	7
440	64	55	40	49	75	52
531	8	0	0	5	9	7

$I_1(\text{exp})$ and $I_2(\text{exp})$ are integral intensities for the sample treated in hydrogen at 320°C for 2 and 8 h, respectively.

Models: I – $\text{Cu}^a\text{Cr}_2^d\text{O}_4$; II – $\text{Cu}^{a,0.5}\text{Cr}_2^d\text{O}_4$; III – $\text{Cu}^{a,0.25}\text{Cu}^c\text{Cr}_2^d\text{O}_4$; IV – $\square^a\text{Cu}_{0.5}^c\text{Cr}_2^d\text{O}_4$ (compensation of the charge by protons is assumed). a, c, d are crystallographic positions of cations in the spinel structure [6,8].

its exposure to hydrogen at 320°C. The study showed only a small increase in the amount of copper metal formed (from 40–50 to 60%)² against the time variation from 2 to 8 h, whereas a considerable redistribution of spinel lines intensity, i.e. a change in the spinel structure, was observed. Therefore, apart from the reduction of the surface to form water which results in no structural change, two alternative processes take place in hydrogen. One of them is completed in the first 2–3 h; it is, apparently, the exchange interaction between hydrogen and copper ions. Another is completed not earlier than in 8 h of the exposure. The nature of the latter may be considered in terms of atomic structure of the reduced chromite.

Table 1 shows integral intensities of the experimental diffraction patterns recorded for the chromite exposed to hydrogen at 320°C as compared to the theoretical ones calculated for vari-

² In all experiments quantitative estimations of the amount of copper metal were done according to [14].

Table 2

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

Atom	Position	Occupation	x	y	z	$B(\text{isot})$
Cu ₁	8a	0.379	0.125	0.125	0.125	2.07
Cu ₂	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

ous models [6]. The comparison makes it possible to suggest a most realistic composition and structure of the reduced chromite. The model, in which 50% of copper ions are removed from the 8a positions and the rest ions are shared between the positions 8a and 16c after 2 h exposure and move completely to the 16c positions after 8 h exposure, seems the most compliant with the experimental data [6,8]. The model was improved in the frame of the space group $Fd\bar{3}m$, $a = 8.348(3)$ Å using the sample exposed to H₂ for 2 h; the composition with the uncertainty factor as low as $R = 0.038$ was thus allowed. The data on occupancy of crystallographic positions, oxygen parameter x , and isotropic heat parameters of atoms of this composition are presented in Table 2. The coincidence of the experimental and theoretical diffraction patterns of the sample exposed to hydrogen for 2 h is seen in Fig. 3.

It is rather difficult to attain more clarity about the structure of the sample reduced for 8 h due to numerous extended defects formed in it.

The states of dissolved hydrogen and their location over the structure of the reduced chromite was studied using a neutronogram recorded for the sample exposed to hydrogen at 320°C for 2 h [16].

From the neutronographic data without considering hydrogen atoms, the structure under examination of the reduced sample has $R = 0.42$, although its theoretical and experimental diffraction patterns coincide with $R = 0.038$. All of the possible hydrogen positions in the cubic spinel structure [8] were analyzed: in the

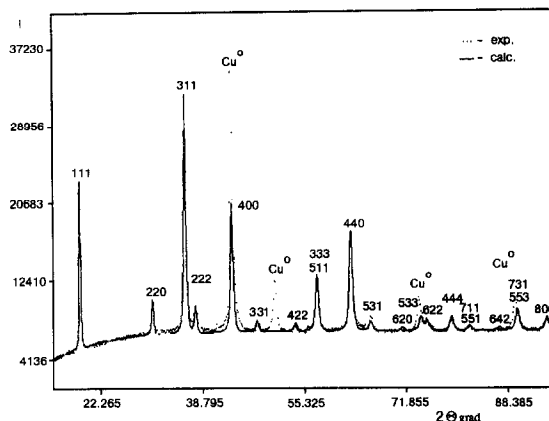


Fig. 3. Experimental X-ray diffraction pattern of the reduced copper chromite and the pattern calculated for the suggested model.

centers of tetrahedrons and octahedrons, at their faces and edges. A significant improvement of the R -factor to 0.093 can be attained for the composition in which hydrogen atoms are located simultaneously at two kinds of positions:

- (1) at 32e positions ($x = 0.1875$) — in tetrahedrons whose centers (8a positions) have been occupied by copper ions before the reduction;
- (2) at 16c positions — at the centers of empty octahedrons of the spinel.

A further improvement of the R -factor to 0.056 was attained by varying the ratio of copper ions occupying 8a positions to those at 16c positions. Coordinates for all the atoms including hydrogen, occupancy of the crystallographic positions, and isotropic heat parameters for the proposed composition are shown in Table 3, and correlations between the experimental

Table 3

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

Atom	Position	Occupation	x	y	z	$B(\text{isot})$
Cu ₁	8a	0.33	0.125	0.125	0.125	1.49
Cu ₂	16c	0.07	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 ₁	32e	0.30	0.187	0.187	0.187	1.03
H ₂	16c	0.38	0	0	0	0.70

diffraction pattern and the calculated one in Table 4.

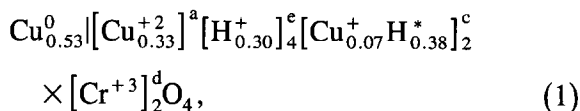
The obtained neutronographic data were analyzed to conclude about the interatomic distances. For hydrogen at tetrahedrons, one H–O distance equal to 0.96 Å and three distances equal to 2.33 Å were shown, while for 16c positions all the six H–O distances are 2.12 Å. Hence, the proton formed as a result of exchange interaction with the copper ion in the tetrahedron reacts with one of the oxygen ions of the tetrahedron to form a covalent O–H bond resembling the H–O–H bonds of a water molecule. The hydrogen of octahedrons cannot be treated as a constituent of such groups as HO[−], H₃O⁺, H₂O but represents a state similar to the atomic state at the oxygen octahedral surrounding. A similar hydrogen state is discussed in [15].

Table 4
The experimental and calculated neutron diagrams for reduced copper chromite (model of cubic spinel structure was used [8])

<i>hkl</i>	2θ(exp) (deg)	<i>I</i> (exp)	<i>I</i> (calc)	2θ(calc) (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	41.63	—	2	41.63
511	44.29	26	29	44.29
333			0	
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	62.40	7	0	62.41
551			5	
642	65.76	4	2	65.76

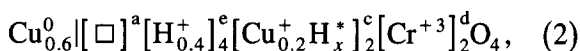
Analysis of the data obtained allows the compositions of the sample exposed to hydrogen to be described as follows:

(a) For the sample exposed for 2 h



where a, c, d, e are the crystallographic positions of ions in the spinel structure [6] and H* stands for occluded hydrogen in octahedral positions.

(b) For the sample exposed for 8 h (if assume that there is no change in hydrogen state as the exposure time increases)



where □ is an unoccupied position and *x* is the proportion (unknown) of the 16c positions occupied by hydrogen.

Thus, the interaction of the copper chromite with hydrogen at 200–400°C is thought to proceed in the following manner.

A portion of surface oxygen ions react with hydrogen to yield water. As a result, reduced copper species (Cu⁺ or Cu⁰) are formed at the chromite surface. Copper species cause a homolytic rupture of the bond in a hydrogen molecule. Hydrogen atoms penetrate into free octahedral positions and copper-containing tetrahedral positions. In the octahedrons hydrogen atoms occupy its centers. In the tetrahedrons the exchange interaction takes place between hydrogen atoms and copper ions to generate protons. The latter form covalent bonds with oxygen atoms of the tetrahedrons. When interacting with two H atoms, copper ions are transformed to their atomic states and released upon the spinel surface where they build-up flat particles bonded epitaxially to the spinel surface. When reacting with one hydrogen atom, the copper ions are reduced to Cu⁺ and move towards the 16c positions. Structural rearrangement which takes place in the course of the chromite reduction is shown in Fig. 4. In the flowing helium there are the back processes — Cu⁰ atoms reduce pro-

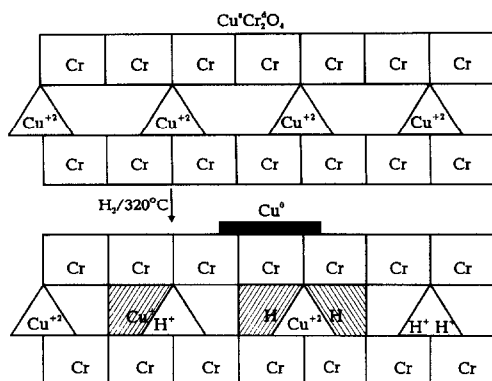


Fig. 4. Schematic presentation of the reversible reduction of copper chromite. Triangles indicate (a) tetrahedral positions; squares indicate (d) octahedral positions; hatched areas indicate (c) octahedral positions.

tions, and Cu ions (probably Cu^{2+} ions) return back to the spinel lattice.

3.1.2. Structure of reduced solid solutions based on anion-modified zinc oxide

More than 1 at% of the Cu^{2+} ions cannot be dissolved in zinc oxide but under certain conditions: zinc oxide with higher copper content can be produced through thermal decomposition of combined hydroxocarbonates at below 500°C . The study of the formation of copper–zinc and copper–zinc–aluminium oxide systems showed that thermal decomposition of copper–zinc and copper–zinc–aluminium hydroxocarbonates proceeds through three stages which are seen in the DTA and DTG curves [16]:

- adsorbed water is released at $120\text{--}140^\circ\text{C}$;
- copper–zinc–aluminium hydroxocarbonates are destructed at $270\text{--}290^\circ\text{C}$ to produce anion-modified oxides (i.e. those containing impurities of OH^- and CO_3^{-2} groups which are the anions of the precursors);
- removal of the impurities and formation of a mixture of stoichiometric oxides (copper oxide, zinc oxide, and spinel in the presence of aluminium) occur at $510\text{--}560^\circ\text{C}$.

The samples prepared at $300\text{--}480^\circ\text{C}$, i.e. the anion-modified oxides, reveal the highest activities. Structural features and composition of these oxides were studied using XRD, EM and analyt-

ical EM techniques. They were shown to be anomalous solid solutions: an imperfectly structured ZnO phase was formed due to the presence of impurity anions, copper ions could occupy the sites at the fault layer superposition. EDRS data [17] show the copper ions to be arranged as small sized clusters and in a flat square oxygen surrounding.

Solid solutions formed in the Cu–Zn samples can involve as many as up to 10 at% of copper and those in the Cu–Al–Zn samples up to 20 at% of copper without CuO phase formation. The solid solutions are formed as a result of substitution of Al^{3+} ions for zinc in ZnO that generates vacancies and increases the content of impurity anions. As the total copper concentration increases further to 60 at%, the content of its clusters in the solid solutions also increases to 25–30 at% for Cu–Zn and 40–45 at% for Cu–Zn–Al samples. Concurrently, the phase of a-m CuO appears and grows in the samples. The chosen compositions, i.e. $\text{Cu}_{0.08}\text{Zn}_{0.92}\text{O}^*$, and $\text{Cu}_{0.15}\text{Zn}_{0.75}\text{Al}_{0.1}\text{O}^*$, provide the samples with no impurity phase involved.

Fragments of diffraction patterns recorded for the initial samples and for those treated with hydrogen at $220\text{--}230^\circ\text{C}$ are presented in Fig. 5a, curves 1–3. A phase of copper metal is seen to appear in hydrogen and disappear in flowing helium. Repeated exposure of the sample to flowing hydrogen results in the appearance of

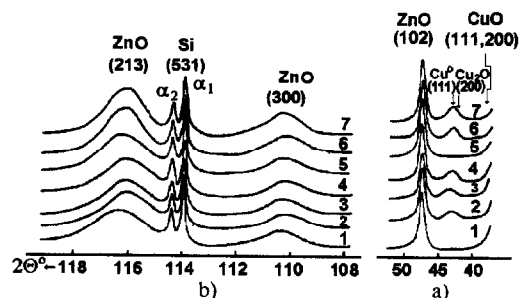


Fig. 5. Fragment of in situ X-ray diffraction patterns. a – $2\theta \sim 40^\circ\text{--}50^\circ$, b – $2\theta \sim 108^\circ\text{--}119^\circ$, of the sample $\text{Cu}_{0.1}\text{Zn}_{0.9}\text{O}^*$ after treatment: 1 – in air at 20°C ; 2 – in hydrogen at 220°C ; 3 – in helium at 220°C ; 4 – in hydrogen at 220°C ; 5 – in $\text{H}_2 + \text{CO}$ mixture at 220°C ; 6 – in hydrogen at 420°C ; 7 – in helium at 420°C .

the Cu^0 phase which disappears again upon substitution of hydrogen for helium (Fig. 5a, curves 4, 5). Reoxidation does not occur in the inert medium after hydrogen treatment at temperatures of 420°C and higher (Fig. 5a, curves 6, 7).

Reoxidation of the sample in the inert medium was confirmed by studying the same fragment using electron microscopy. The microdiffraction data show the epitaxial junction of copper metal formed in hydrogen and zinc oxide growing along the direction of $[001]\text{ZnO}[[111]\text{Cu}^0]$. Epitaxial interaction of Cu^0 with ZnO in a reduced sample was observed before [18], while its reoxidation in an inert medium was not reported. Fig. 5b shows a fragment of the diffraction pattern recorded at the 2θ range of 108–119° where the spots (300) and (213) of ZnO and (531) of Si reference were observed. There is practically no change in the lattice constant a of the reduced sample, whereas constant c appears to be sensitive to the state of the solid solution. Compared to constant c of ZnO, constant c of the solid solution decreases for its oxidized state; upon sample reduction it approximates that for ZnO and decreases again upon the reoxidation in flowing He (Table 5).

The results obtained are considerable evidence for the Cu^0 phase to be formed on the surface of the reduced sample as a result of reduction of copper ions of the solid solution and to come back to the bulk of the solid solution during their reoxidation. Evidently, these processes are the consequence of the exchange interaction with protons involved:

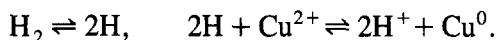
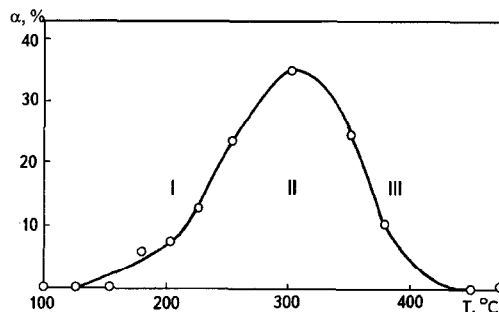


Table 5

Lattice constants of Cu-containing ZnO after thermal treatment in various media

Thermal treatment conditions	a (Å) $\Delta a = \pm 0.002$	c (Å) $\Delta c = \pm 0.003$	Phase composition
Air, 350°C	3.250	5.194	$\text{Cu}_{0.08}\text{Zn}_{0.92}\text{O}^*$
Hydrogen, 220°C	3.254	5.217	$\text{Cu}_x^0 + \text{Cu}_{(1-x)}^{0.08}\text{Zn}_{0.92}\text{O}^*$
Helium, 220°C	3.252	5.202	$\text{Cu}_{0.08}\text{Zn}_{0.92}\text{O}^*$

* Anion modified oxide.

Fig. 6. Conversion of acetone to isopropanol at 75°C versus the temperature of copper chromite pretreatment with H_2 .

The process becomes irreversible when the protons form water by a high temperature reaction with hydroxyls or when Cu^0 is oxidized by O_2 (see Fig. 1).

3.2. Mechanisms for hydrogenation of the C–O bond in carbon oxides and acetone

To elucidate the mechanisms for hydrogenation of acetone to isopropanol and for synthesis of methanol from carbon oxides, the interaction of catalysts activated by hydrogen with the compounds to be hydrogenated was studied.

3.2.1. Hydrogenation of acetone to isopropanol

Catalytic properties of copper chromite were studied using a pulse flow installation at 75°C; the reaction products were identified chromatographically. This reaction temperature was chosen so that the effect of the back reaction becomes negligible. A mixture of 10 vol% of acetone in hydrogen was examined. The catalyst was preactivated in hydrogen at various temperatures. Fig. 6 shows the conversion of acetone

to isopropyl alcohol versus the temperature of hydrogen pretreatment of the sample.

Three activation temperature ranges at which the catalyst reveals different properties can be revealed. There is observed practically no conversion of acetone to isopropanol over the catalyst treated with hydrogen at temperatures below 120–150°C. At a higher reduction temperature isopropanol is formed, and the conversion of acetone increases as the temperature increases, the maximum conversion being observed at 300–350°C. The further increase in the reduction temperature results in a lower yield of isopropanol, which becomes zero above 420–430°C.

As mentioned above, the state of copper chromite in the hydrogen medium depends on temperature. The reversible (when helium is substituted for H₂) state exists at 200–400°C. This state is a spinel with two above described types of hydrogen species dissolved in it; the flat copper metal particles are formed on its surface. It is seen in Figs. 1, 2 and 6 that this is the only state of chromite which catalyzes hydrogenation of acetone to isopropanol.

The interaction of acetone with copper chromite pretreated with hydrogen at 300°C was studied. The conversion of acetone to isopropanol was shown to take place after supplying acetone pulses to the reduced catalyst in the absence of hydrogen in gas phase. The rate of the formation of isopropanol decreases as the absorbed hydrogen is consumed, and becomes low in rather short time. The starting rate of the reaction of acetone with absorbed hydrogen (Fig. 7) depends on the temperature of preactivation of copper chromite with hydrogen; this dependence resembles the dependence of the copper chromite activity for the reaction between acetone and gaseous hydrogen on prerduction temperature (Fig. 6): the highest activity is observed with the sample reduced at 300°C. Besides, the starting rate of the formation of isopropanol at 300°C in the absence of hydrogen ($1.2\text{--}1.4 \times 10^{-6} \text{ mol/m}^2 \cdot \text{s}$) is close to the rate of the steady-state reaction of acetone and hy-

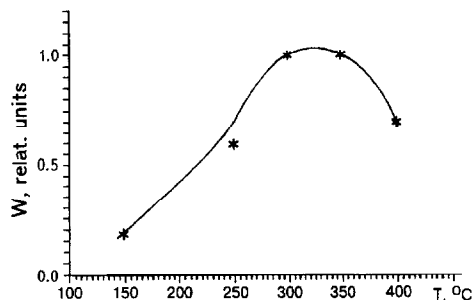


Fig. 7. The initial rate of isopropanol formation in the absence of hydrogen in relative units versus the temperature of the catalyst prerduction (the rate for the sample prerduced at 300°C was used as a standard). The reaction mixture was '10 vol% acetone + helium'.

drogen. The latter was found using the gradientless method to be $1.0 \times 10^{-6} \text{ mol/m}^2 \cdot \text{s}$ for a mixture containing 10 vol% acetone in hydrogen at 300°C [19].

In situ XRD technique was used at 75°C to study the interaction of acetone with copper chromite reduced at 300–320°C. When the mixture of acetone in helium is passed through, the amount of copper metal on the chromite surface decreases and a spinel restores its initial structure. Further treatment of the sample with hydrogen results in restoring the reduced state of the chromite which is capable of catalyzing hydrogenation of acetone to isopropanol with the same activity.

The results obtained allow to conclude that it are protons dissolved in spinel which are responsible for catalytic hydrogenation of acetone to isopropanol.

The phenomena observed by us, viz.: (1) reversibility of the system at medium variations of $\text{H}_2 \rightarrow \text{He} \rightarrow \text{H}_2$; (2) bulk absorption of hydrogen, at least a noticeable proportion (corresponding approximately to a half of the total of copper in the chromite) of which is as protons, that makes it possible to consider the reduced chromite to be a solid solution of chromic acid and copper chromite, i.e. 'solid protonic medium'; (3) formation of isopropyl alcohol as a result of interaction of acetone with the reduced catalyst; (4) transformation of the re-

duced catalyst to its oxidized state under the action of acetone, allow to discuss the mechanism of the reaction under study in terms of ideas developed for liquid-phase reduction of ketones to alcohols with metals soluble in a 'protonic medium' [20].

According to these ideas, hydrogenation proceeds in the following manner (Fig. 8): electrons of the metal and proton of the solution are accepted by a molecule of ketone. The organic molecule becomes negatively charged, and the second proton is added. Based on numerous experimental data obtained and literature data [20–22], the following scheme can be proposed for hydrogenation of acetone over copper chromite (Fig. 9):

At the first stage the reduced state of chromite is formed upon the reversible interaction with hydrogen that results in dissolving protons in the spinel. A corresponding amount of Cu^0 as epitaxially bonded flat particles is released at the surface.

The second stage is hydrogenation of acetone. According to [22], acetone is adsorbed on Cu^0 atoms as π -complexes, electrons of the metal transfer to antibonding π -orbitals of the carbonyl group. Concurrently, a proton of the reduced chromite is inserted into an adsorbed acetone molecule. As a result, the organic molecule acquires a negative charge, and copper metal is oxidized and occupies the positions in the spinel structure it has left during the reduction. These transformations are followed by in-

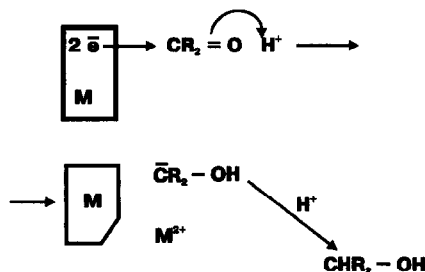


Fig. 8. Schematic presentation of the mechanism of liquid-phase hydrogenation of ketones to alcohols catalyzed by metals soluble in a 'protonic medium' [20].

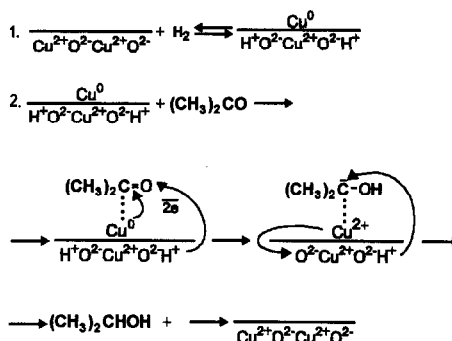


Fig. 9. Schematic presentation of acetone hydrogenation to isopropanol.

sertion of the second proton from the chromite and desorption of an alcohol molecule.

As shown, the catalyst is in its reduced state under the reaction conditions; hence, the second stage can be assumed to be the rate limiting. Under the conditions of catalytic hydrogenation, when there are both acetone and hydrogen in the reaction medium, it is most likely that only the protons located on the surface layer are involved in the transformations. Correspondingly, the reversible conversion of copper metal to its ionic state occurs only within the spinel surface layer.

3.2.2. Synthesis of methanol

Activity of the catalyst (solid solution of copper ions both in a-m ZnO and Al-containing a-m ZnO) for synthesis of methanol is in proportion to the content of copper up to 30 at%. With 30–45 at% of copper, it is close to the activity of the most active catalysts. That was why the solid solutions of copper ions in a-m ZnO of the compositions $\text{Cu}_{0.08}\text{Zn}_{0.92}\text{O}^*$ and $\text{Cu}_{0.15}\text{Zn}_{0.75}\text{Al}_{0.1}\text{O}^*$ were chosen for the studies.

3.2.2.1. Interaction of reduced solid solution with reactants

Interaction with carbon monoxide. The in situ XRD technique was used for studying the phase composition changes of reduced catalyst in CO-containing medium. When a mixture of 5 vol% of CO in nitrogen was passed over the

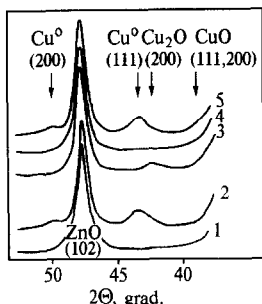


Fig. 10. X-ray patterns of $\text{Cu}_{0.08}\text{Zn}_{0.92}\text{O}^*$: 1 – initial state; 2 – treated with H_2 at 220°C ; 3 – sample 2 treated with CO_2 at 220°C during 2 h; 4 – and during 4 h; 5 – sample 2 treated with CO_2 and then CO during 2 h.

reduced catalyst at 220°C , the phase composition of the catalyst varied like it does in flowing helium, i.e. the catalyst restored its initial oxidized state. The outlet gas mixture contained no methanol.

Interaction with carbon dioxide. Fig. 10 shows fragments of the diffraction pattern recorded for the initial (curve 1) and reduced (curve 2) copper–zinc samples kept in flowing CO_2 at 220°C for 2 h (curve 3) and for 4 h (curve 4) until the diffraction pattern ceased changing.

The state of reduced catalyst changes in a complex fashion under the action of CO_2 (Fig. 11). During the first two hours the copper metal phase decreases and disappears completely. Concurrently, a Cu_2O phase appears and its amount increases. Under the action of CO_2 for another 2 h the Cu_2O phase decreases to its practical disappearance. The constant c of the a-m ZnO lattice treated with CO_2 reaches that of the oxidized sample, i.e. the initial structure is restored. The same transformations are observed upon further alternative treatment of the sample with hydrogen and CO_2 .

The outlet reaction mixture contained methanol along with CO_2 during the first two hours of the treatment and, practically, only water after another two hours. Hence, the interaction of CO_2 with the reduced catalyst produces methanol. The reaction proceeds through the interaction with dissolved proton and oxida-

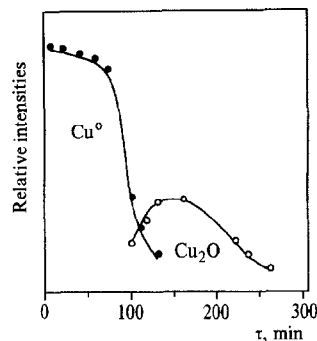
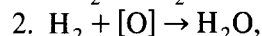
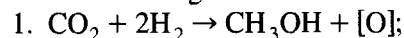


Fig. 11. The changes of relative intensities of (111) Cu^0 and (200) Cu_2O reflections for a sample $\text{Cu}_{0.08}\text{Zn}_{0.92}\text{O}$ prereduced by hydrogen at 220°C versus the time of treatment with CO_2 at 220°C .

tion of copper metal particles to Cu_2O followed by the interaction of oxygen of the oxide and protons to form water. Thus, the reaction of methanol synthesis from CO_2 and H_2 , which is described by the equation



proceeds in two stages, the second of which is the rate limiting one:



where $[\text{O}]$ is a surface oxygen ion.

Interaction of the catalyst, activated by hydrogen and treated with carbon dioxide, with carbon monoxide and $\text{CO} + \text{H}_2$ mixture. Fig. 10, curve 5, represents a fragment of the diffraction pattern recorded for the reduced catalyst after its successive exposure to flowing CO_2 for two hours and to a mixture of 5 vol% of CO in nitrogen to obtain the unchanged diffraction pattern (for another two hours). The mixture was switched to the catalyst at the instant when the copper metal phase was practically completely transformed to Cu_2O (curve 3). The exposure of the catalyst to the flowing CO -containing mixture results in a decrease in the amount of cuprous oxide during the first half an hour (since CO cannot oxidize copper), and the copper metal phase becomes observable (curve 5). The outlet reaction mixture contained methanol (gas probes were picked up during the

first hour). When the flow of $\text{CO} + \text{H}_2$ was substituted for $\text{CO} + \text{N}_2$, the Cu_2O phase disappeared too, and the copper metal was observed; in this case the amount of methanol formed increased.

Therefore, methanol is formed as a result of the interaction of CO with the catalyst pretreated with hydrogen and CO_2 but not of the interaction of CO with the reduced catalyst. Thus, methanol can be synthesized through hydrogenation of both CO_2 and CO , but in the latter case the catalyst must be pretreated with carbon dioxide.

Apparently, the rate of methanol synthesis from CO and the rate of the first stage of methanol synthesis from CO_2 are close to each other, while the overall rate of methanol synthesis from CO_2 is limited by a slower stage of water formation. It is true if the rate of CO adsorption on reduced and pretreated with CO_2 catalyst is large enough not to be limiting.

It is interesting that the authors of [23] observed the formation of oxygen ions on the surface of a reduced copper-containing catalyst upon feeding CO_2 to the catalyst. They reported

the dependence of the activity for methanol synthesis on the surface oxygen coverage: the activity increases in proportion to the coverage of below 0.16 monolayer, keeps constant up to 0.18 monolayer, and decreases with the further increase in the surface oxygen content.

From what has been said it may be possible to describe the principal steps of the scheme for methanol synthesis as follows (Fig. 12):

(1) Reversible interaction of the solid solution of Cu^{2+} in a-m ZnO with hydrogen to generate the reduced state of the catalyst which is the solid solution in which a proportion of copper ions is substituted for protons, and the corresponding amount Cu^0 is located as an epitaxially bonded phase over the surface.

(2) Adsorption of CO_2 on copper metal particles and its interaction with protons to produce methanol and oxygen-containing sites of the $\text{Cu}^{+1}\text{-O-Cu}^{+1}$ type on the metal particle surface. Methanol is evidently formed through a semihydrogenated intermediate of the type of $[\text{:CHOH}]$ by means of transfer of protons from the solid solution surface and electrons from Cu^0 towards the adsorbed CO_2 , like it was

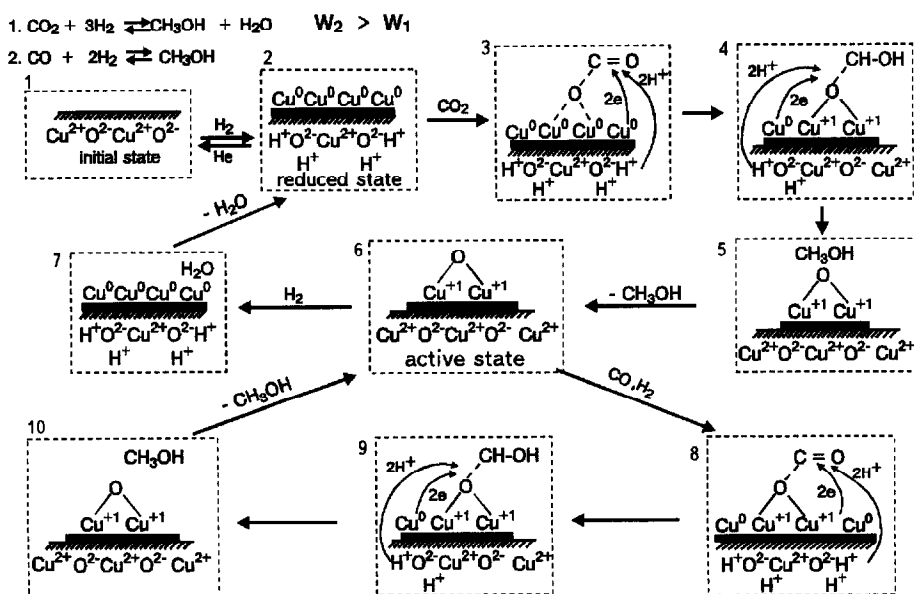


Fig. 12. Schematic presentation of the mechanism of the methanol synthesis.

suggested for hydrogenation of acetone over chromite. Copper ions formed return in the solid solution.

(3) Interaction of the oxygen-containing sites in the reaction medium along two paths:

(a) CO is adsorbed on an oxygen ion as a fragment whose structure resembles the structure of the fragment formed upon adsorption of CO₂ on the metal ions. As a result, the CO molecule is rapidly hydrogenated to methanol as described above, the oxygen site being unchanged and capable again of activating CO molecules.

(b) Oxygen ions interact with hydrogen to form water and Cu⁰, the oxygen site disappearing.

The rate ratio for these paths determines the ratio of the rate of the formation of methanol from CO to that from CO₂. Apparently, the overall rate of methanol formation is to a great extent determined by the rate of CO hydrogenation; however CO hydrogenation is not possible but in the presence of CO₂ which provides generation of the oxygen-containing sites.

The catalyst in its reduced state, in which the metal particles have the oxygen-containing sites on their surface, should be discussed more carefully. This is an intermediate state formed during the reaction of methanol synthesis from CO₂ and H₂: the oxygen-containing sites appear during the formation of methanol and disappear at the interaction with protons or other activated hydrogen species to form water. However, this is the active state of the catalyst for synthesis of methanol from CO and H₂. The formation of water causes destruction of CO activation sites.

Based on the data obtained, the questions by catalytic chemists engaged in the synthesis of methanol [24–26]:

- Is methanol formed from CO or CO₂?
- Which is the active state of copper: metallic or ionic? can be answered in the following way.

Synthesis of methanol can be achieved with both CO₂ and CO as a feedstock, although the latter case needs the presence of CO₂.

There are three stages of methanol synthesis from CO₂:

- generation of protons and Cu⁰;
- formation of methanol and oxygen containing sites on the catalyst surface;
- formation of water through interaction of hydrogen with the oxygen ions of the above sites.

The last stage is the rate limiting. This is evident from Cu₂O phase formation under the action of CO₂ on reduced catalyst.

Synthesis of methanol from CO in the presence of CO₂ is a three-stage process, too:

- generation of protons and Cu⁰;
- formation of oxygen-containing sites on the metal surface after the interaction with CO₂;
- formation of methanol.

As to the active state of copper, one can say that copper ions are active in oxide compounds in which they can be reduced to metal under the action of hydrogen to generate protons and be oxidized upon the interaction of protons with the molecules hydrogenated.

4. Conclusions

The results obtained allow the conclusion that two copper-containing oxides of different natures, copper chromite and anomalous solid solutions of Cu²⁺ ions in a-m ZnO, behave similarly for the interaction with hydrogen at temperatures of below 400–450°C. The oxides dissolve hydrogen, which is partially consumed to reduce copper ions of the oxide and transformed to protons; the copper ions form a Cu⁰ phase epitaxially bonded to the oxide surface. Removal of hydrogen causes the reverse processes, i.e. protons are reduced to reoxidize copper, hydrogen is desorbed, copper ions come back to the oxide structure.

Hydrogenation of carbon oxides and acetone is the result of the ability of copper ions to reversible transformations to generate copper metal and protons.

Activation of the molecules to be hydrogenated may occur on Cu^0 directly. This is the case of hydrogenation of acetone over the reduced copper chromite and hydrogenation of CO_2 over the reduced solid solution of copper ions in a-m ZnO. Alternatively, this may happen on the sites formed through interaction of copper ions with reactants, like it is observed for synthesis of methanol from CO over oxygen-containing sites of the $\text{Cu}^{+1}\text{-O-Cu}^{+1}$ type generated through oxidation of copper Cu^0 with CO_2 at the surface of the reduced solid solution of copper ions in a-m ZnO.

Generally speaking, it is possible that both types of dissolved hydrogen species, protons and 'activated atoms', can be involved in the hydrogenation reactions. However, the discussed hydrogenation of the C–O bond over copper-containing catalysts involves protons, while electrons are transferred from Cu^0 and copper ions come back into the oxide structure. The 'activated atoms' of hydrogen can be imagined to be capable of, e.g., forming C–H bonds or hydrogenating C=C bonds of hydrocarbons.

Acknowledgements

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