

# Evolution of Cu–Zn–Si Oxide Catalysts in the Course of Reduction and Reoxidation as Studied by In Situ X-Ray Diffraction Analysis, Transmission Electron Microscopy, and Magnetic Susceptibility Methods

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**Abstract**—The reduced and reoxidized Cu–Zn–Si oxide catalysts as layered copper–zinc hydroxo silicates with the zincsilite structure were studied using in situ and ex situ X-ray diffraction analysis, transmission electron microscopy, and the temperature dependence of magnetic susceptibility. The catalysts were prepared by homogeneous deposition–precipitation. It was found that Cu<sup>0</sup> particles were formed on the surface of a layered hydrosilicate with the zincsilite structure upon reduction with hydrogen. The reoxidation of the reduced samples with a mixture of oxygen and an inert gas, which contained no more than 0.05 vol % O<sub>2</sub>, resulted in the formation of individual Cu<sub>2</sub>O and CuO phases; copper ions did not return to the hydrosilicate structure. Catalytic tests of Cu–Zn–Si catalysts in methanol synthesis indicate that the specific catalytic activity of copper metal particles grows linearly with increasing zinc loading. This fact suggests that copper metal particles, which were obtained by the reduction of Cu<sup>2+</sup> ions from the copper–zinc hydroxo silicate with the zincsilite structure, were responsible for activity in methanol synthesis. Consequently, the ability to return copper ions to a precursor compound in reoxidation with oxygen at low concentrations, which is known for reduced Cu/ZnO catalysts (these catalysts are highly active in methanol synthesis), is not related to the catalytic activity in methanol synthesis.

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## INTRODUCTION

Traditionally, copper-containing catalysts are considered as the most efficient catalysts for methanol synthesis. Currently, it is believed that the presence of a copper metal phase is a necessary condition for the high activity of catalysts. Earlier, Chinchin et al. [1] assumed that the specific activity of copper metal was constant in catalysts with structurally and chemically different supports. However, a number of studies performed more recently suggest a considerable role of the support. It was found [2, 3] that the specific activity of copper metal in Cu–Si oxide catalysts was much lower than that in Cu–Zn oxide catalysts. A decrease in the catalytic activity of Cu<sup>0</sup> in the order Cu<sup>0</sup>/ZnO > Cu<sup>0</sup>/Al<sub>2</sub>O<sub>3</sub> > Cu<sup>0</sup>/SiO<sub>2</sub> was also found [4]. Copper metal prepared from a mixed Cu–Zn hydroxo compound exhibited a higher activity. The mixing of a Cu–Si oxide catalyst precursor with a Zn–Si hydroxo compound resulted in an increase in its specific activity [5]. Fujitani et al. [6] noted a considerable change in the

specific activity of Cu<sup>0</sup> upon the introduction of Al, Ga, Zr, and Cr cations into a support with the ZnO structure. Note that the nature of the support affects the activity of copper in other reactions, for example, methanol dehydrogenation [7] and ether hydrogenolysis [3].

There is no clarity as to the cause of the effect of the structure and composition of the support on the specific activity of copper metal (see review [8]). It was found that even an insignificant change in the redox potential of the gas phase considerably affected the state of the active component of a Cu/ZnO catalyst. The introduction of an oxidizing agent (CO<sub>2</sub> or H<sub>2</sub>O) into synthesis gas resulted in a decrease in the adhesion of the metal to zinc oxide. This manifested itself in changes in the habitus of copper metal particles and in the type of predominant faces on the surface of these particles [9, 10]. In our opinion, the previously found ability of the active component of Cu/ZnO catalysts to undergo reversible transformation under the action of a reaction mixture [9–12] deserves special attention. The reversible

**Table 1.** Cation composition of Cu–Zn–Si catalysts and the specific surface area of copper metal after reduction in hydrogen at various temperatures

Catalyst	Cation composition, at %			$S_{\text{Cu}}$ , m <sup>2</sup> /g		
	Cu	Zn	Si	reduction temperature, K		
				653	710	900
CS	14.0	0	86.0	14.2	15.2	–
CZS4	14.0	4.0	82.0	14.0	14.4	–
CZS7	14.6	7.7	77.7	17.3	17.9	–
CZS12	14.6	12.0	73.4	16.3	17.9	4.5
CZS15	14.6	15.0	70.4	13.8	14.6	1.7
CZS20	14.6	20.0	65.4	15.2	11.2	–
CZS30	12.8	30.0	57.2	11.8	5.4	–

change in the phase composition of a catalyst manifests itself in the reduction of copper ions from a mixed oxide  $\text{Cu}_x\text{Zn}_{1-x}\text{O}$  with the formation of epitaxially bound copper metal particles and the return of copper cations to the structural defects of zinc oxide in the course of oxidation with oxygen at low concentrations [11, 12]. Such changes in the active component under the action of the reaction atmosphere were not observed in copper-containing catalysts supported on  $\text{SiO}_2$  [4]. In this context, it is believed that the reversible reduction of copper cations from an oxide precursor and the change in the habitus of active metal particles under the action of the reaction atmosphere are essential features of active catalysts for methanol synthesis.

The aim of this work was to study the state of copper atoms in Cu–Zn–Si oxide catalysts after their successive treatment with hydrogen and oxygen in an inert gas ( $\leq 0.05$  vol %  $\text{O}_2$ ). Because the Cu–Zn–Si oxide catalysts exhibit noticeable activity in methanol synthesis, data on the observed structural changes can be useful for supporting or refuting the previous hypothesis on a relationship between the activity of copper-containing catalysts in methanol synthesis and their ability to undergo reversible reduction to an active state and the return to the structure of a mixed copper-containing oxide upon reoxidation in the presence of oxygen in low concentrations.

## EXPERIMENTAL

**Sample preparation.** The test samples were prepared by homogeneous deposition–precipitation on  $\text{SiO}_2$  from copper nitrate and zinc nitrate solutions in the presence of urea [13, 14]. A suspension of Aerosil 300 in water and corresponding amounts of zinc nitrate (Donetsk chemical reagent factory, Ukraine;  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  content, >98%) and copper nitrate (Saki chemical reagent factory, Ukraine;  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  content, >99%) with urea (Cherkassy chemical reagent factory, Ukraine; urea content, >99%) were heated at 90°C for 20 h with continuous stirring.

After the completion of precipitation, the precipitate (a catalyst precursor compound) was filtered off and washed with hot water on a filter. Then, the sample was dried and calcined in a flow of air at 723 K. Table 1 summarizes the cation composition of the resulting samples.

According to Yurieva et al. [14], the preparation procedure resulted in the complete chemical interaction of components with the formation of copper hydrosilicates (with the chrysocolla structure) and copper–zinc hydrosilicates with the zincsilite structure. Note that a layered silicate with the zincsilite structure is characterized by high thermal stability and its treatment at temperatures lower than 973 K resulted in the removal of only a portion of interlayer water without considerable structural changes. Khassin et al. [15] found that the layered zinc silicate  $\text{Zn}_3[\text{Si}_4\text{O}_{10}](\text{OH})_2 \cdot n\text{H}_2\text{O}$  decomposed with the formation of zinc orthosilicate  $\text{Zn}_2\text{SiO}_4$  (willemite) at 1063 K. At lower temperatures, water was gradually removed from the interlayer space accompanied by a decrease in the interlayer distance.

According to Yurieva et al. [16], the structure of Cu–Zn silicates did not decompose up to 923–973 K even in a reducing atmosphere, that is, after the reduction of copper cations as the constituents of a layered silicate. This observation formed a basis for the hypothesis on the reoxidation of copper with the return of cations to the structure of a layered silicate; this hypothesis is considered in this paper.

**X-ray diffraction data.** The X-ray diffraction (XRD) data were obtained on a Siemens D-500 diffractometer. The diffraction patterns were measured using monochromated  $\text{CuK}\alpha$  radiation with a graphite monochromator in the reflected beam by scanning over the  $2\theta$  angle range of 15°–65° at a step  $\tau = 0.05^\circ$  and an accumulation time of 5 s at each point.

A series of in situ measurements was performed in a reactor chamber of the Siemens D-500 diffractometer in a flow of hydrogen (5 l/h) at a heating rate of 2 K/min. After keeping the catalyst at a specified tem-

perature with an unchanged diffraction pattern, as monitored by measuring the  $\text{Cu}^0$  (111) line intensity (referred to as  $\text{CZS-R}_{in}(T_{\text{red}})$ ), the samples were reoxidized in a flow of helium containing 0.05 vol %  $\text{O}_2$  (referred to as  $\text{CZS-RO}_{in}(T_{\text{reox}})$ ).

The samples for a series of ex situ experiments were reduced in a flow system in a flow of hydrogen (3–5 l/h) at a heating rate of 2 K/min. Then, the samples were kept at a specified temperature for 2 h (referred to as  $\text{CZS-R}_{ex}(T_{\text{red}})$ ). The reduced samples were reoxidized in a flow of argon containing ~0.05 vol %  $\text{O}_2$  (referred to as  $\text{CZS-RO}_{ex}(T_{\text{reox}})$ ).

Henceforth, the term *reoxidation* means treatment in an inert gas flow containing no more than 0.05 vol %  $\text{O}_2$ .

**Thermal analysis.** Thermal analysis was performed using a Netzsch STA-409 thermogravimetric analyzer at a heating rate of 10 or 5 K/min in flowing argon (150  $\text{cm}^3/\text{min}$ ) and hydrogen (150  $\text{cm}^3/\text{min}$ ), respectively; the catalyst sample weight was 50–100 mg.

**Specific surface area of copper metal.** The specific surface area of copper metal was determined by pulsed titration with  $\text{N}_2\text{O}$  using chromatographic analysis. The surface area of copper metal was calculated assuming that an oxygen atom is equivalent to two surface atoms of copper metal. The surface density of copper atoms was set at  $1.46 \times 10^{19}$  atom/ $\text{m}^2$  (the average value for the Cu (100), (110), and (111) faces).

**IR spectra.** The IR spectra were recorded using a Bomem MB-102 FTIR spectrometer over the range 300–4000  $\text{cm}^{-1}$ . A powdered catalyst was mixed with KBr, and pellets were pressed.

**Sample micrographs.** The micrographs of samples were obtained on a JEM-2010 transmission electron microscope with a resolution of 1.4 Å. The samples were prepared by ultrasonic dispersion in alcohol and supporting onto perforated carbon substrates.

**Temperature dependence of magnetic susceptibility.** The temperature dependence of magnetic susceptibility was studied by the Faraday method over the temperature range of 78–300 K at an external magnetic field strength of 10.9 kOe. In the calculation of the molar magnetic susceptibility ( $\chi$ ), the diamagnetism of atoms was taken into consideration in accordance with the Pascal additivity law. The effective magnetic moment was calculated as  $\mu_{\text{eff}} \approx (8\chi T)^{1/2}$ .

**Catalytic properties.** The catalytic properties were tested in a plug-flow reactor 16 mm in diameter at a pressure of 2 MPa over a temperature range of 423–543 K. The reactor was loaded with 2 g of a catalyst with a particle size of 0.25–0.5 mm. Before loading, the catalyst granules were mixed with quartz granules of the same particle size in a volume ratio of 1 : 1. The catalysts were activated in hydrogen at 653 K. The flow rate of the reaction gas was 6 l/h; the gas composition was  $\text{CO}/\text{H}_2/\text{CO}_2 = 22 : 76 : 2$ . The composition of reaction products was analyzed by gas chromatography with a flame-ionization detector. The activity was characterized by the rate constant per unit surface area of

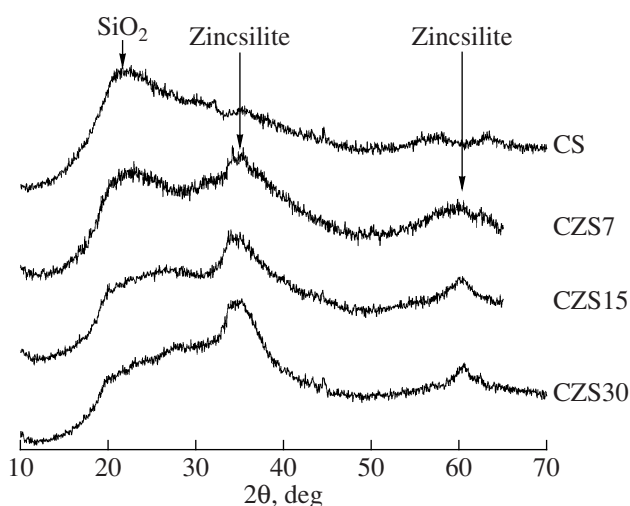


Fig. 1. Diffraction patterns from catalyst precursors.

copper metal. The calculations were performed assuming a plug-flow reactor, a reaction of first order with respect to CO, and a unimolecular rate-limiting step.

## RESULTS AND DISCUSSION

### Characterization of Catalyst Precursors

Figure 1 shows the diffraction patterns from the initial samples of precursor compounds. Diffuse halos due to  $\text{SiO}_2$  in the  $2\theta$  region of  $\sim 20^\circ$ – $23^\circ$  and the most intense lines due to zinc hydrosilicate, zincsilite  $\text{Zn}_3[\text{Si}_4\text{O}_{10}](\text{OH})_2 \cdot n\text{H}_2\text{O}$  (JCPDS 29-1393), with  $d_{006} = 2.56$  Å and  $d_{300} = 1.53$  Å can be seen ( $hkl$ ) are given for a hexagonal packing in space group  $P6$ ).

Zincsilite has a layered structure. The three-layer packing is formed by two layers of oxygen tetrahedrons and a layer of octahedrons between them. Zinc ions are localized in octahedral positions. The packs are separated by the interlayer space with zinc ions coordinated to water molecules. Thus, with consideration for different positions of  $\text{Zn}^{2+}$  ions, zincsilite is described by the formula  $\text{Zn}_x(\text{Zn}_{3-x}\square_x)[\text{Si}_4\text{O}_{10}](\text{OH})_2 \cdot n\text{H}_2\text{O}$ , where  $[\text{Si}_4\text{O}_{10}]$  is the layer of  $\text{Si}^{4+}$  in oxygen tetrahedrons,  $\square$  is the ion vacancy,  $\text{Zn}_{3-x}$  are ions in the octahedral positions of the packs, and  $\text{Zn}_x$  are ions in the interlayer space. It is well known that copper cations can replace zinc cations in the zincsilite structure. The Cu/Zn ratio in the zincsilite structure can be as high as 0.5 [16].

A broad asymmetric reflection at  $2\theta = 35^\circ$  ( $d = 2.56$  Å) is a superposition of several unresolved lines due to silicate; among them, (006) is the main line. Poor line resolution was observed in all of the test samples, and it suggested a low degree of crystallinity. As the zinc content of the sample was increased, the zincsilite line intensity increased and the intensity of the halo due to  $\text{SiO}_2$  decreased. Characteristic reflections from the copper oxide phases  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  were absent from the

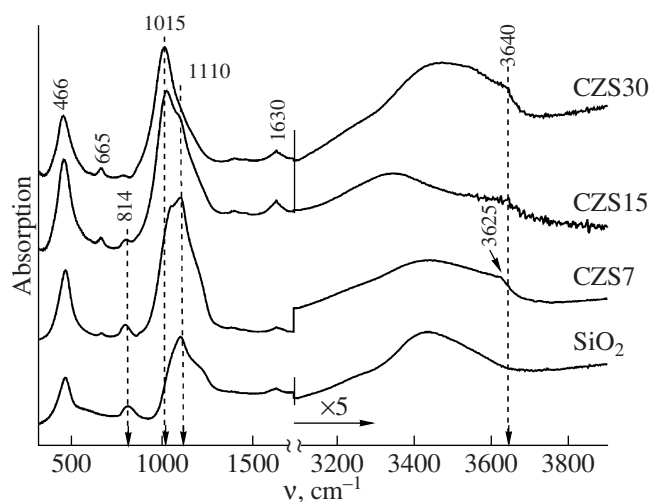


Fig. 2. IR spectra of catalyst precursors.

diffraction patterns. It is likely that a portion of copper cations forms an X-ray amorphous copper silicate with the chrysocolla-like structure  $\text{Cu}_2\text{H}_2(\text{Si}_2\text{O}_5)(\text{OH})_4 \cdot n\text{H}_2\text{O}$  rather than entering into the structure of zincsilite. Copper and zinc hydrosilicates can be distinguished by the vibration frequency of OH groups. This frequency is 3625 or 3640  $\text{cm}^{-1}$  for copper hydrosilicate with the chrysocolla structure or zinc hydrosilicate with the zincsilite structure, respectively [14]. Figure 2 shows the IR spectra of the initial samples of Cu–Zn–Si oxide catalysts. It can be seen clearly that the observed vibrational energy of OH groups increased from 3625 to 3640  $\text{cm}^{-1}$  in the series of samples as the zinc content was increased. This is consistent with the above hypothesis on the distribution of copper cations between the phase with the chrysocolla structure, which was predominant in sample CZS7, and the phase with the zincsilite structure, which was predominant in sample CZS30. In the spectra of samples with lower zinc contents, absorption bands that were attributed to  $\text{SiO}_2$  (1110 and 814  $\text{cm}^{-1}$ ) occurred in addition to the absorption bands of a layered silicate with the  $\text{Si}_4\text{O}_{10}$  structure-forming group (about 1015 and 466  $\text{cm}^{-1}$ ) and Me–O vibrations (about 665  $\text{cm}^{-1}$ ). Evidently, this can be explained by the excess silicon content of the sam-

**Table 2.** Results of a magnetic susceptibility study and estimated fractions of copper in the state of isolated  $\text{Cu}^{2+}$  cations [ $\text{Cu}_{\text{isol}}^{2+}$ ] for the precursors of Cu–Zn–Si oxide catalysts

Catalyst	$C$ , $\text{cm}^3 \text{ K mol}^{-1}$	$\Theta$ , K	$\mu_{\text{eff}}$ , $\mu_B$	$[\text{Cu}_{\text{isol}}^{2+}]$
CZS7	0.053	–10.1	0.644	0.99
CZS15	0.056	–6.28	0.665	1.00
CZS30	0.047	–6.90	0.605	0.98

ples, as compared with the stoichiometry of layered silicates.

Additional information on the state of copper can be obtained from the temperature dependence of magnetic susceptibility. Indeed, weakly interacting with each other (isolated)  $\text{Cu}^{2+}$  ( $d^9$ ) cations are paramagnetic with  $\mu_{\text{eff}}(\text{Cu}^{2+}, 300 \text{ K}) = 1.73\mu_B$ , whereas  $\text{Cu}^+$  ( $d^{10}$ ) cations are diamagnetic. The magnetic susceptibility of strongly interacting  $\text{Cu}^{2+}$  cations in the CuO phase is low at temperatures higher than room temperature because CuO is an antiferromagnet with the Neel temperature ( $T_N$ ) of 220 K and  $\mu_{\text{eff}}(\text{CuO}, 300 \text{ K}) = 0.8 \mu_B$ .

From the experimental results, it follows that the starting samples were paramagnetic materials and the temperature dependence of the magnetic susceptibility ( $\chi$ ) of these materials obeyed the Curie–Weiss law with the parameters specified in Table 2:

$$\chi = \frac{C}{T - \theta}. \quad (1)$$

The Curie constant ( $C$ ) allowed us to evaluate the amount of  $\text{Cu}^{2+}$  cations that were not the constituents of CuO, that is, the cations in hydrosilicate structures. The theoretical value of  $\mu_{\text{eff}}$  for sample CZS30 containing 12.8 at % copper was  $0.62\mu_B$ , and the corresponding value for samples CZS15 and CZS7 containing 14.6 at % copper was  $0.66\mu_B$ . As can be seen in Table 2, the experimental values of  $\mu_{\text{eff}}$  are very close to the theoretical values. Consequently, it is believed that all of the copper atoms occurred in the  $\text{Cu}^{2+}$  state and did not enter into the composition of CuO. A small negative value of the Weiss constant ( $\theta$ ) suggests a weak antiferromagnetic interaction of cations with each other, which is consistent with the system of  $\text{Cu}^{2+}$  cations distributed in the structure of a Zn–Si hydroxo compound or chrysocolla.

Thus, the samples prepared by homogeneous deposition–precipitation contained a mixture of highly dispersed oxo–hydroxo silicate compounds:  $(\text{Cu,Zn})_3[\text{Si}_4\text{O}_{10}](\text{OH})_2 \cdot n\text{H}_2\text{O}$  (a copper–zinc hydrosilicate with the zincsilite structure),  $\text{Cu}_2\text{H}_2(\text{Si}_2\text{O}_5)(\text{OH})_4 \cdot n\text{H}_2\text{O}$  (an X-ray amorphous copper hydrosilicate with the chrysocolla structure), and amorphous silica. The fraction of silicon cations that form a hydrosilicate with the zincsilite structure increased with the zinc content of the sample. Copper cations occurred in the  $\text{Cu}^{2+}$  state and entered into the composition of hydrosilicates, whereas CuO was not formed.

#### Catalytic Properties of Cu–Zn–Si Oxide Catalysts

Based on published data [16], it is believed that a considerable degree of reduction of copper cations from the structure of chrysocolla or a layered zinc hydrosilicate was reached at 483 or 653 K, respectively. Below, we will consider in detail the behavior of catalysts from the CZS system on reduction and reoxidation over a wide range of temperatures. However, the depen-



**Table 3.** Results of a study of methanol synthesis on Cu–Zn–Si oxide catalysts

Sample	493 K				523 K			
	$X_{\text{CH}_3\text{OH}}$ , vol %	$Y_{\text{CH}_3\text{OH}}$ , $\text{g g}_{\text{Cat}}^{-1} \text{h}^{-1}$	$\Pi/K_p$	$k^{\rightarrow}$ , $\text{cm}^3 (\text{NTP}) \text{m}^{-2} \text{s}^{-1}$	$X_{\text{CH}_3\text{OH}}$ , vol %	$Y_{\text{CH}_3\text{OH}}$ , $\text{g g}_{\text{Cat}}^{-1} \text{h}^{-1}$	$\Pi/K_p$	$k^{\rightarrow}$ , $\text{cm}^3 (\text{NTP}) \text{m}^{-2} \text{s}^{-1}$
CS	0.28	0.011	0.0072	$6.26 \times 10^{-5}$	1.27	0.049	0.16	$3.31 \times 10^{-4}$
CZS4	0.37	0.013	0.011	$7.77 \times 10^{-5}$	0.96	0.034	0.12	$2.28 \times 10^{-4}$
CZS7	0.59	0.023	0.016	$1.09 \times 10^{-4}$	1.37	0.052	0.17	$2.90 \times 10^{-4}$
CZS12	1.25	0.048	0.034	$2.65 \times 10^{-4}$	2.54	0.098	0.33	$6.81 \times 10^{-4}$
CZS15	1.47	0.058	0.041	$3.13 \times 10^{-4}$	2.79	0.11	0.37	$7.62 \times 10^{-4}$
CZS20	1.62	0.066	0.045	$3.97 \times 10^{-4}$	2.92	0.12	0.39	$9.23 \times 10^{-4}$
CZS30	1.05	0.041	0.029	$3.07 \times 10^{-4}$	2.80	0.11	0.39	$1.06 \times 10^{-3}$

Note:  $X_{\text{CH}_3\text{OH}}$  is the concentration of methanol;  $Y_{\text{CH}_3\text{OH}}$  is the yield of methanol;  $\Pi/K_p$  is the ratio of the product of the component fugacities to the equilibrium constant, which characterizes the approach of the reaction to an equilibrium; and  $k^{\rightarrow}$  is the rate constant of the forward reaction of methanol synthesis.

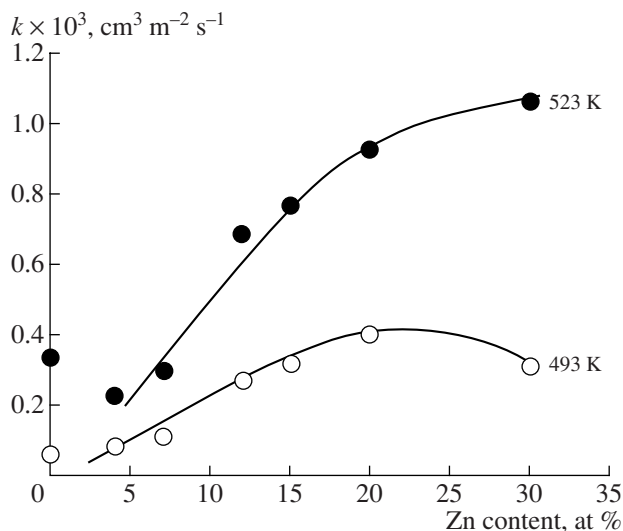
dence of the catalytic properties of Cu–Zn–Si oxide catalysts on the concentration of zinc in them should initially be noted. Table 1 summarizes the results of the measurements of the specific surface area of copper metal for CZS catalysts reduced in a flow of hydrogen at 653 and 710 K. The experimental data suggest that highly dispersed copper metal particles were formed upon the reduction of the Cu–Zn–Si oxide catalysts. Taking into account that the extent of copper reduction was about 60%, as measured by the magnetic susceptibility method (see below), we estimated the metal particle size at 4–5 nm. Note that the introduction of zinc into the parent silicate did not have a considerable effect on the specific surface area of  $\text{Cu}^0$  in the samples reduced at 653 K. At the same time,  $\text{Cu}^0$  particles prepared by the reduction of chrysocolla (sample CS) did not agglomerate at temperatures lower than 710 K. Evidently, activation at 900 K resulted in the sintering of metal particles.

Table 3 summarizes the results of the study of catalytic properties in methanol synthesis at 493 and 523 K and a pressure of 2 MPa with a working gas containing  $\text{CO}$ ,  $\text{H}_2$ , and  $\text{CO}_2$  in a ratio of 22 : 76 : 2. The activity was characterized by the reaction rate constant per unit surface area of  $\text{Cu}^0$ . Table 3 also summarizes the  $\Pi/K_p$  ratios, which characterize the approach of the reaction to equilibrium (here,  $\Pi$  is the product of the component fugacities at the reactor outlet to the powers of their stoichiometric numbers).

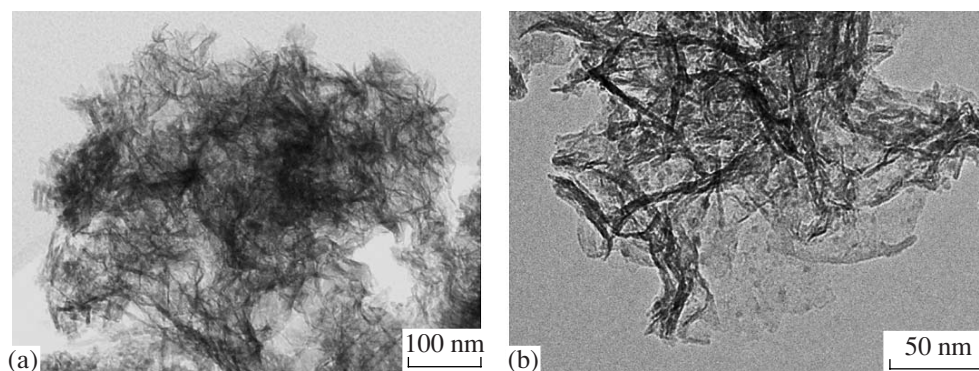
Figure 3 shows the dependence of the activity on the zinc content of Cu–Zn–Si oxide catalysts. The activity linearly increased with the zinc content. As discussed above, an increase in the concentration of zinc in the catalyst resulted in an increase in the concentration of a phase with the zincsilite structure; the formation of other zinc-containing compounds was not observed

both in the hydroxo precursor of the catalyst and after the reductive activation.

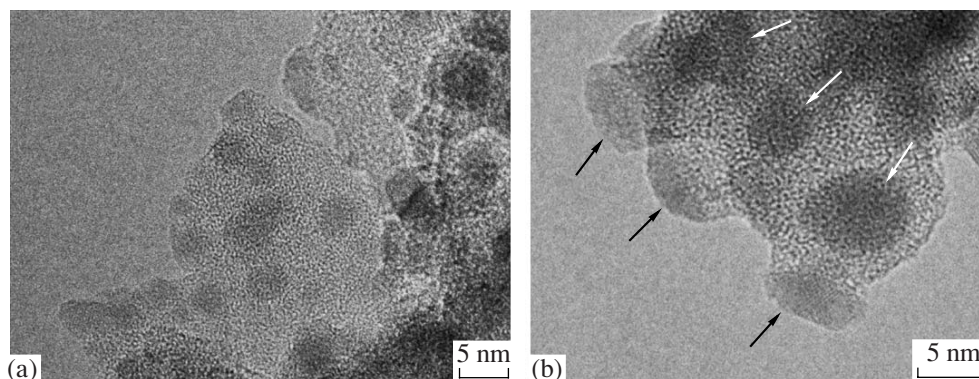
Note that the reaction rate constants were referenced to the specific surface area of copper metal; therefore, they characterized the averaged activity of  $\text{Cu}^0$  in the sample. Copper metal particles in the ternary system differed in the nature of precursor compounds: some particles were formed as a result of the reduction of copper hydrosilicate (chrysocolla), and the others resulted from the reduction of copper cations from a zinc hydrosilicate with the zincsilite structure. All of the particles had approximately the same size, but the fraction of particles produced by the reduction of zinc-



**Fig. 3.** Dependence of the specific rate constant of the forward reaction of methanol synthesis on the zinc content of Cu–Zn–Si catalysts reduced at 653 K ( $P = 2$  MPa;  $\text{CO}/\text{H}_2/\text{CO}_2 = 22 : 76 : 2$ ).



**Fig. 4.** Micrographs of (a) the precursor of sample CZS30 and (b) catalyst CZS30 after reduction in a flow of  $H_2$  at 523 K and reoxidation at 543 K (sample CZS30-RO<sub>in</sub>543).



**Fig. 5.** Micrographs of (a) catalyst CZS30 after reduction in a flow of  $H_2$  at 523 K (sample CZS30-R<sub>in</sub>523) and (b) sample CZS30-R<sub>in</sub>523 subjected to the action of an electron beam. White and black arrows indicate  $Cu^0$  and ZnO particles, respectively.

silite increased with increasing zinc content. Thus, it is believed that the catalytic activity depends on the amount of copper particles formed by the reduction of copper cations from layered zinc–copper hydrosilicate with the zinsilite structure.

The behavior of copper cations in the reduction and reoxidation of three-component catalysts was studied.

#### *Evolution of Cu–Zn–Si Oxide Catalysts in the Course of Reduction and Reoxidation According to Transmission Electron Microscopic Data*

The precursors of CZS catalysts consisted of thin flat particles 20–100 nm in length and 5–6 nm in thickness. The layered structure of these particles can be seen clearly in micrographs (see Fig. 4). Copper metal particles with a size of 2–3 nm can be detected in the micrographs of catalysts reduced at 523 K (see the image of sample CZR30-R<sub>in</sub>523 in Fig. 5a); in this case, the layered zinsilite structure was retained. Note that being in air in the course of sample preparation for studies did not result in the oxidation of copper metal. As the reduction temperature was increased to 623 K, the particle size of copper increased to 5 nm. Note that

the sample rapidly changed its structure under the action of a high-intensity electron beam. The layered support structure degraded, and particles of a well-crystallized zinc oxide phase appeared (see Fig. 5b). This is additional evidence for the occurrence of zinc cations as the constituents of a layered silicate in the initial sample.

Note that the reoxidation of catalysts at 543 K did not change the pattern: contrast particles of ~3 nm were observed against the background of the layered structure. The measurement of atomic spacings in electron diffraction patterns allowed us to identify these particles as  $Cu_2O$  and  $CuO$ . At the same time, the state of particles can change under the action of an electron beam; therefore, the observed particles cannot be ascribed to the copper metal phase or the oxide phases  $Cu_2O$  and  $CuO$  based on transmission electron microscopic data. The presence of copper metal or copper oxide particles after reoxidation suggests that the return of copper cations to the zinsilite structure did not occur or occurred incompletely. After reoxidation at 673 K, contrast particles of 4–5 nm in size, which corresponds to the particle size of copper metal after sample reduction at 623 K, were retained in the sample (see

Fig. 4b). The hypothesis of irreversibility was quantitatively supported using magnetic methods and XRD analysis.

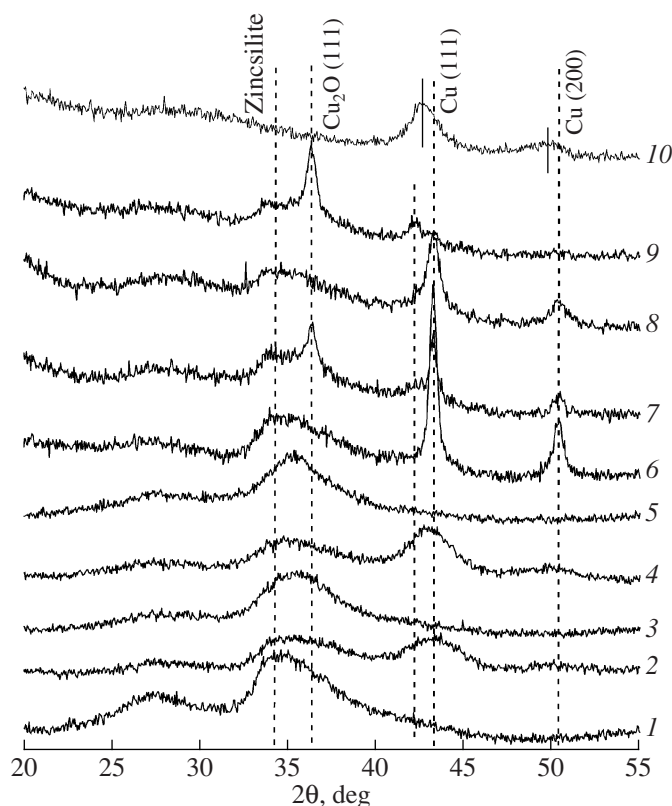
#### Reduction of Cu–Zn–Si Catalysts as Studied by XRD

According to Yurieva et al. [16], the characteristic temperatures of copper reduction from the chrysocolla structure, the interlayer space of the zincsilite structure, and the octahedral positions in a zincsilite layer are 463, 503–533, and 623–653 K, respectively. In this work, the samples were reduced at the above temperatures. Additionally, the reduction was performed at 700 and 873 K. Figure 6 shows the diffraction patterns of sample CZS30, which was reduced and reoxidized at different temperatures.

A copper metal phase occurred in all of the reduced samples (see characteristic diffraction peaks at  $2\theta = 43.32^\circ$  ( $d_{111} = 2.09 \text{ \AA}$ ) and  $50.45^\circ$  ( $d_{200} = 1.81 \text{ \AA}$ ), which correspond to diffraction from the (111) and (200) planes of the fcc structure of  $\text{Cu}^0$  (JCPDS-04-0836)). Based on the integrated width of these X-ray lines for sample CZS30- $R_{in}(523)$ , the size of the coherent-scattering region (CSR) can be estimated at 3–4 nm. An increase in the reduction temperature to 653 K increased the integrated line intensity by a factor of 1.4, as compared with sample CZS30- $R_{in}(523)$ , and decreased the bandwidths by a factor of about 1.3. Evidently, this suggests an increase in both the particle size and the fraction of copper converted into the metal state. Based on these estimations, we can assume that new nucleation centers of copper metal particles, if any, occurred in an insignificant amount as the reduction temperature was increased. The newly reduced copper atoms were mainly involved into existing particles. These results are consistent with XRD data for an analogous sample [16].

The diffraction patterns of reduced samples CZS30- $R_{in}(523)$ , CZS30- $R_{in}(653)$ , CZS30- $R_{ex}(653)$ , and CZS30- $R_{ex}(700)$  retained lines characteristic of the zincsilite structure; however, the intensity of these lines decreased, as compared with that of the initial sample. This suggests that copper cations that were the constituents of copper-containing zincsilite were reduced.

The  $\text{Cu}^0$  diffraction lines in the diffraction pattern of the sample CZS30- $R_{ex}(873)$  shifted to smaller angles. The line width corresponded to the CSR size of metal particles of about 7 nm, and the observed shift corresponded to an increase in the lattice parameter  $a(\text{Cu}^0)$  from 3.627 to 3.663 Å. It is reasonable to assume that zinc ions from the silicate structure were partially reduced with the formation of a copper and zinc alloy. Assuming that the lattice parameter of a Cu–Zn solid solution obeys the Vegard law (is a linear function of the mole fraction of zinc) and the distances are  $R_{\text{Cu–Cu}} = 2.556 \text{ \AA}$  and  $R_{\text{Zn–Zn}} = 2.665 \text{ \AA}$ , we can evaluate the zinc content of an alloy at ~24 at %. This value is consistent in terms of the order of magnitude with the thermody-



**Fig. 6.** Diffraction patterns from (1–5) in situ and (6–10) ex situ catalysts CZS30: (1) precursor, (2)  $R(523)$ , (3)  $RO(543)$ , (4)  $R(653)$ , (5)  $RO(673)$ , (6)  $R(653)$ , (7)  $RO(653)$ , (8)  $R(700)$ , (9)  $RO(700)$ , and (10)  $R(873)$ .

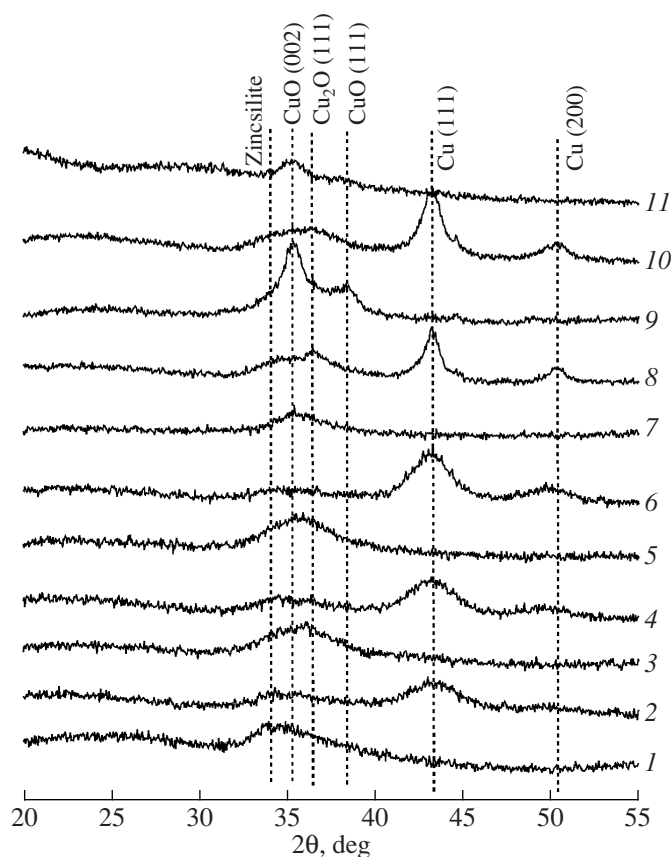
amic estimations of brass formation in the reduction of the Cu/ZnO system in a flow of hydrogen (12% at the ratio  $\text{H}_2/\text{H}_2\text{O} = 1000$ ) [17]. Note that diffraction reflections from the zincsilite structure were not observed in the diffraction pattern; this fact suggests the degradation of the copper–zinc hydrosilicate structure. At the same time, a halo in the region  $2\theta = 30^\circ$  was present; this suggests the formation of a new silicon-containing compound. The results for samples CZS15 and CZS7 (Figs. 7, 8) are similar to the above data for sample CZS30.

The general views of diffraction patterns obtained both ex situ and in situ were analogous. However, note that the CSR size for copper metal particles was much greater for ex situ samples and reached 14 nm. It is likely that the low rate of gas supply in ex situ reduction resulted in local sample overheating and, as a consequence, in the agglomeration of copper metal particles.

#### XRD Data on the Reoxidation of Cu–Zn–Si Catalysts in a Flow of an Inert Gas Containing 0.05% $\text{O}_2$

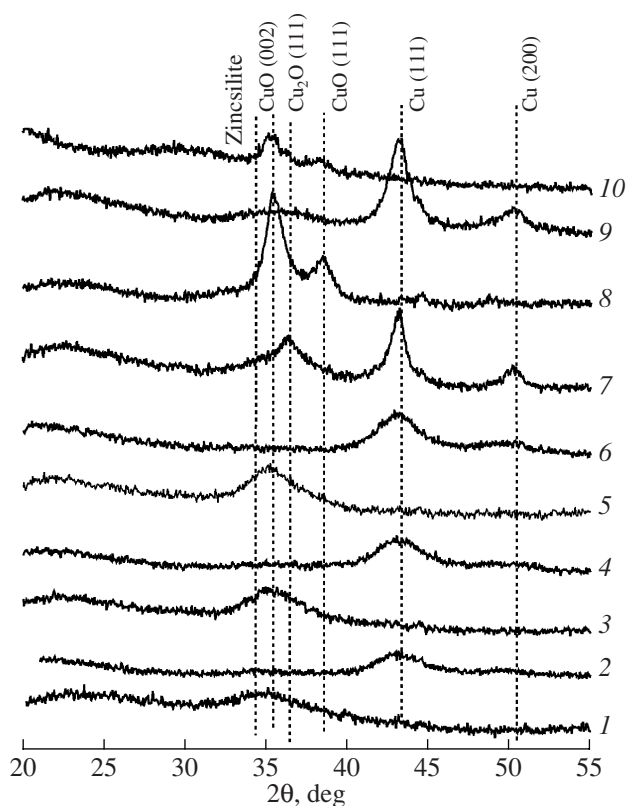
The lines corresponding to copper metal were absent from the diffraction patterns of samples CZS30- $RO_{in}(543)$  and CZS30- $RO_{in}(673)$  (Fig. 6), and the line





**Fig. 7.** Diffraction patterns from (1–7) in situ and (8–11) ex situ catalysts CZS15: (1) initial, (2) R(463), (3) RO(483), (4) R(503), (5) RO(543), (6) R(623), (7) RO(653), (8) R(653), (9) RO(653), (10) R(700), and (11) RO(700).

intensity at  $2\theta = 35^\circ$  recovered. Note a considerable change in the line shape and the shift of the peak position of the complex line attributed to the layered silicate (zincsilite) in the initial samples toward larger angles. The simultaneous appearance of a halo at  $2\theta \sim 42.3^\circ$  (for  $\text{Cu}_2\text{O}$   $d_{200} = 2.12 \text{ \AA}$ ) allowed us to attribute this shift to the formation of a dispersed phase of  $\text{Cu}_2\text{O}$  in the course of reoxidation. In this case, the shift of the zincsilite line can be explained by the appearance of a diffraction line from  $\text{Cu}_2\text{O}$  with a characteristic intensity maximum at  $2\theta = 36.4$  ( $d_{111} = 2.43 \text{ \AA}$ ) (JCPDS 34-1354). The formation of  $\text{Cu}_2\text{O}$  can be seen especially clearly in the diffraction patterns of samples subjected to ex situ treatments. The line due to  $\text{Cu}^0$  was retained in the diffraction pattern of CZS30-RO<sub>ex</sub>(653), but its integrated intensity decreased upon reoxidation. In this case, a line due to  $\text{Cu}_2\text{O}$  at  $d_{111} = 2.43 \text{ \AA}$  can be seen clearly and a halo at  $d_{200} = 2.12 \text{ \AA}$  can be detected. Reoxidation at a higher temperature resulted in the disappearance of a line due to  $\text{Cu}^0$  with a simultaneous increase in the integrated intensity of a band due to  $\text{Cu}_2\text{O}$  in CZS30-RO<sub>ex</sub>(700). Thus,  $\text{Cu}^0$  changed to the state  $\text{Cu}^+$  in reoxidation and the return of copper ions to the zincsilite structure did not occur.



**Fig. 8.** Diffraction patterns from (1–6) in situ and (7–10) ex situ catalysts CZS7: (1) precursor, (2) R(463), (3) RO(473), (4) R(503), (5) RO(533), (6) R(623), (7) R(653), (8) RO(653), (9) R(700), and (10) RO(700).

The diffraction patterns of in situ catalysts CZS15 and CZS7 with low zinc contents after reoxidation had analogous shapes (Figs. 7, 8). In the ex situ reoxidation of these catalysts, deeper copper oxidation to  $\text{CuO}$  occurred, as evidenced by characteristic diffraction lines with  $d_{002} = 2.52 \text{ \AA}$  and  $d_{111} = 2.33 \text{ \AA}$  (JCPDS 05-661). Thus, it is believed that  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  are formed in reoxidation without the return of copper ions to the zincsilite structure.

#### *Study of the Temperature Dependence of the Magnetic Susceptibility of Reduced and Reoxidized Cu–Zn–Si Oxide Catalysts*

Both reduced and reoxidized Cu–Zn–Si catalysts are paramagnetic materials, whose magnetic susceptibility obeys Curie–Weiss law (1) with the parameters specified in Table 4.

Because only  $\text{Cu}^{2+}$  ( $d^9$ ) ions make a paramagnetic contribution to magnetic susceptibility, the magnetic moment of such a compound is zero in the case of the complete reduction of the above ions. The fraction of  $\text{Cu}^{2+}$  paramagnetic centers  $x_{\text{Cu(II)}}$  can be determined as the square of the ratio of  $\mu_{\text{eff}}$  of the reduced sample to the



**Table 4.** Results of a magnetic susceptibility study and estimated fractions of copper in the state of isolated  $\text{Cu}^{2+}$  cations [ $\text{Cu}_{\text{isol}}^{2+}$ ] for the reduced and reoxidized Cu–Zn–Si oxide catalysts

Sample	Reduction in $\text{H}_2$					Reoxidation in an inert gas containing 0.05 vol % $\text{O}_2$				
	$T, \text{K}$	$\mu_{\text{eff}}^{300}, \mu_{\text{B}}$	$C, \text{cm}^3 \text{K mol}^{-1}$	$\theta, \text{K}$	$[\text{Cu}_{\text{isol}}^{2+}]$	$T, \text{K}$	$\mu_{\text{eff}}^{300}, \mu_{\text{B}}$	$C, \text{cm}^3 \text{K mol}^{-1}$	$\theta, \text{K}$	$[\text{Cu}_{\text{isol}}^{2+}]$
CZS30	523	0.516	0.036	–29.6	0.73	540	0.524	0.037	–33.6	0.75
	653	0.377	0.017	–4.7	0.39	653	0.428	0.023	–4.3	0.50
	700	0.378	0.022	–64.5	0.39	700	0.376	0.018	–4.9	0.39
	873	0.268	0.0095	–16.1	0.20					
CZS15	463	0.580	0.043	–10.2	0.76	483	0.571	0.043	–20.4	0.74
	503	0.569	0.043	–21.5	0.73	543	0.590	0.045	–11.7	0.79
	623	0.457	0.029	–35.2	0.47					
	653	0.412	0.022	–10.1	0.38	653	0.494	0.033	–25.8	0.55
CZS7	700	0.354	0.017	–32.2	0.28	700	0.502	0.035	–51.3	0.57
	463	0.510	0.036	–37.3	0.63	473	0.549	0.043	–48.4	0.73
	503	0.541	0.042	–46.3	0.71	503	0.518	0.036	–36.8	0.65
	653	0.418	0.023	–25.4	0.42	653	0.473	0.033	–75.0	0.54
	700	0.377	0.020	–39.3	0.34	700	0.474	0.035	–85.3	0.54

corresponding value of the reduced calcined sample:  $x_{\text{Cu(II)}} = \mu_{\text{eff}}(\text{red})^2/\mu_{\text{eff}}(\text{init})^2$  (in the case of reoxidized samples,  $x_{\text{Cu(II)}} = \mu_{\text{eff}}(\text{reox})^2/\mu_{\text{eff}}(\text{init})^2$ ). Table 4 summarizes the resulting values of  $x_{\text{Cu(II)}}$ .

In the initial state,  $x_{\text{Cu(II)}} = 1$ . The decrease in the value of  $x_{\text{Cu(II)}}$  as the reduction temperature was increased was consistent with the increase in the fraction of copper cations reduced to the metal state. Note that, even at very high reduction temperatures ( $\geq 700 \text{ K}$ ), a considerable fraction of copper ions ( $\sim 28\%$ ) remained unreduced. Even after the degradation of the zincsilite structure (sample CZS30- $\text{R}_{\text{ex}}$ 873), the value of  $x_{\text{Cu(II)}}$  was 0.2. This supports the above hypothesis that a new silicon-containing compound, which likely also contained copper ions, was formed in the course of layered silicate degradation. Reoxidation after reduction at 463, 503, and 523 K did not considerably affect the parameter  $x_{\text{Cu(II)}}$ , as compared with the value obtained in reduced samples. This fact suggests that copper remained in the states  $\text{Cu}^0$  or  $\text{Cu}^+$ , which also did not contribute to magnetization. However, if the oxidation of copper to  $\text{Cu}^{2+}$  will be accompanied by the formation of a bulk  $\text{CuO}$  phase, which is an antiferromagnet with the Neel temperature of about 220 K and does not markedly contribute to the magnetization of the sample, the magnetic susceptibility will also not increase.

Reoxidation at 623–653 K performed after corresponding reduction resulted in an increase in  $x_{\text{Cu(II)}}$  to 0.54–0.61. However, this increase is not a consequence of the increase in the amount of isolated  $\text{Cu}^{2+}$  ions, but it should be related to the formation of a  $\text{CuO}$  phase in the oxidation of copper metal. Indeed, as mentioned

above, the value of  $\mu_{\text{eff}}(\text{CuO}, 300 \text{ K})$  is  $0.8\mu_{\text{B}}$ . Consequently, the formation of  $\text{CuO}$  in the amount of 61 at % based on the total copper content (12.8 at %) in catalyst CZS30 after its reoxidation at 653 K should increase  $\mu_{\text{eff}}$  to  $0.44\mu_{\text{B}}$ , which was observed experimentally. Analogous estimations of  $\mu_{\text{eff}}$  for reoxidized samples CZS15- $\text{RO}_{\text{ex}}$ 653 and CZS7- $\text{RO}_{\text{ex}}$ 653 are  $0.48\mu_{\text{B}}$ , which is also consistent with experimental values. Note that samples subjected to successive reduction and reoxidation at 700 K (CZS15- $\text{RO}_{\text{ex}}$ 700 and CZS7- $\text{RO}_{\text{ex}}$ 700) exhibited greater magnetic moments than that estimated from a model of the formation of  $\text{CuO}$ , which predicted the values of 0.45 and  $0.44\mu_{\text{B}}$ , respectively. One reason might be the interaction of an oxidized state of copper with an amorphous silicate phase, the formation of which was hypothesized above based on the presence of a halo in the region of  $27^\circ$ – $30^\circ$  in XRD patterns.

## CONCLUSIONS

The tests of Cu–Zn–Si oxide catalysts in methanol synthesis at 653 K and 2 MPa demonstrated that the activity of  $\text{Cu}^0$  in the samples containing no zinc and with low zinc contents was low, and it linearly increased with the concentration of zinc in the catalyst, that is, with increasing concentration of copper–zinc hydroxo silicate. This suggests that copper particles obtained by the reduction of  $\text{Cu}^{2+}$  cations from a copper–zinc hydroxo silicate with the zincsilite structure are mainly responsible for the activity of the Cu–Zn–Si catalysts in methanol synthesis.

The study performed using XRD analysis (in situ and ex situ), transmission electron microscopy, and magnetic susceptibility measurements demonstrated that the reoxidation of Cu<sup>0</sup> particles formed on the surface of a layered hydrosilicate with the zincsilite structure upon reduction with hydrogen resulted in the formation of independent Cu<sub>2</sub>O and CuO oxide phases rather than the return of copper ions to the hydrosilicate.

A comparison between data obtained in this work and the results of a study on the reversibility of the reduction of copper cations in a Cu/ZnO model catalyst, which exhibited high activity in the reaction of methanol synthesis, as well as the demonstration of the reversibility of the reduction of copper cations in copper chromite CuCr<sub>2</sub>O<sub>4</sub> [18], which was inactive in methanol synthesis, led us to the conclusion that the reversibility of the reduction of copper cations from an oxide precursor does not correlate with catalytic activity in methanol synthesis.

At the same time, the above conclusions cannot deny the importance of interactions between copper particles and the support for the synthesis of methanol. Moreover, data on the dependence of the specific catalytic activity of Cu–Zn–Si oxide catalysts on the composition and structure of a precursor compound suggest a considerable effect of the support on the catalytic properties of copper metal.

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