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Planar defect of the nano-structured zinc oxide as the site for stabilization of the copper active species in Cu/ZnO catalysts

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Abstract

The catalytic activity of CuZn catalysts in the synthesis of methanol is related to those reduced Cu species, which originate from the $Cu_xZn_{1-x}O$ solid solution of wurtzite-like structure. Copper cations in the $Cu_xZn_{1-x}O$ solid solution are localized in the extended stacking faults of the ZnO lattice. Copper sites could be supposedly described as the product of introducing (OH)···Cu···(OH) to the planar defects of zinc oxide structure. Hydroxyl groups stabilize the planar defects of ZnO. The process of the samples reduction leads to the formation of flat Cu^0 particles over the surface of zinc oxide. The planar defects of ZnO structure are preserved in the reduced state. During the reoxidation, copper atoms return back to the extended stacking faults of ZnO as the tape-like clusters of flat-square coordinated copper cations.

Keywords: Cu/ZnO catalyst; Methanol synthesis; Planar defect in oxides; High-resolution electron microscopy; EXAFS spectroscopy

1. Introduction

Cu-Zn and Cu-Zn-Al catalysts are very selective and active enough for the methanol synthesis at low-pressure conditions. A variety of techniques were applied by numerous researchers for studying the reduced state of the Cu-Zn and Cu-Zn-Al catalysts. But the nature of the active sites is still debatable in literature. The present article discusses the nature of stabilizaton of active copper species in a model copper-zinc catalyst oxide precursor. Attention is paid to the interaction of copper species with ZnO-like structure for the Cu-Zn samples, incl. the oxide precursor, as well as those activated in H_2 and after mild re-oxidation.

2. Experimental

Samples of Cu-Zn catalysts were prepared by the calcinations of the Cu-Zn hydroxycarbonates in flowing air at 623 K for 4 h. Hydroxycarbonate precursors of Cu-Zn catalysts were synthesized via the continuous coprecipitation method starting from solution of sodium carbonate and mixture of appropriate quantities of 0.5 M aqueous solutions of Cu and Zn nitrates at 343–348 K and pH 6.9. The precipitates were thoroughly washed to remove Na^+ and NO_3^- ions, filtered out, and dried under IR-lamp overnight. The sodium content is less than 0.01 wt.% as determined by AAS.

Catalytic activity was studied in a continuous circulated flow reactor at 0.1 MPa, 493 K, reaction mixture composition $H_2:CO:CO_2 = 75:20:5$, grain size 0.5–1.0 mm. The catalytic activity was compared at methanol concentration of 10^{-3} vol.%. No by-product was detected at these conditions. At longer contact time and higher CO_x conversion extent, we detected some traces of methylformate.

Reductive treatments were performed in H_2 at 473 K for 1 h, heating rate—2 K min^{-1}. The re-oxidations were performed in the flowing mixture of He and 0.05% O_2 at 2 K min^{-1}, 523 K until the termination of oxygen absorption.

High-resolution electron micrographs were obtained with JEM-2010 instrument with lattice resolution 1.4 Å at accelerating voltage 200 kV. Samples were fixed on ''holey'' carbon films supported on copper or molybdenum grids and investigated with the electron microscope. K edges of copper absorption were obtained by the transmission mode at the EXAFS Spectroscopy Station of Siberian Synchrotron

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Radiation Center (Novosibirsk). The cut-off Si(1 1 1) monocrystal was used as monochromator. Proportional ionization chambers were used as detectors. The oxidized samples were studied in air as tablets. The reduced samples from the reactor were transferred to sealed tubes with beryllium windows to prevent contacting with air. The spectra were taken at room temperature. Metallic copper, CuO and Cu_2O were chosen as model compounds of the known structure. The oscillating part was extracted using the VIPER program. FEFF7 program was employed to fit the scattering parameters. EXAFS spectra were processed for $\kappa^3\chi(k)$ in the range of wave numbers 2.5–12 $Å^{-1}$ with the aid of the VIPER program [1]. Data filtering was not applied.

3. Results and discussion

3.1. Catalytic activity in methanol synthesis

The activity of the Cu-Zn catalysts prepared by the co-precipitation of mixed hydroxycarbonates followed by their calcination and reduction depends significantly on the copper content as one can see from Fig. 1. It increases linearly with the copper content up to 40 at.% but declines with further increasing copper loading. This tendency is close to that reported in [2]. The samples with high loading exhibit also lower thermal stability (see curve 2).

Earlier studies [3,4] of the phase composition of the coprecipitated Cu-Zn samples after their calcination at moderate temperatures (below 725 K) showed that Cu-Zn samples with less than 10–15 at.% of copper don't contain CuO phase, but only ZnO-like phase exists in their composition. At copper loading above 80 wt.%, the samples contain traces of wurtzite-like phase [4] and are not active in the methanol synthesis (see Fig. 1). In the intermediate composition range, tenorite-like Cu(Zn)O phase co-exists with wurtzite-like Zn(Cu)O structure. The enhancement in amount of Cu^{2+} species dissolved in ZnO coincides with the growth of aurichalcite precursor reaching maximum at copper loading of ca. 40 at.% [4].

Thus, the stable active sites of methanol synthesis seems to relate with the reduced Cu species, which originate from the solid solution of Cu^{2+} in wurtzite-like ZnO structure, $Cu_xZn_{1-x}O$. It is noteworthy that only the samples with copper content less than 15 at.% are one-phase $Cu_xZn_{1-x}O$, while those with higher copper content contain tenorite-like oxide phase.

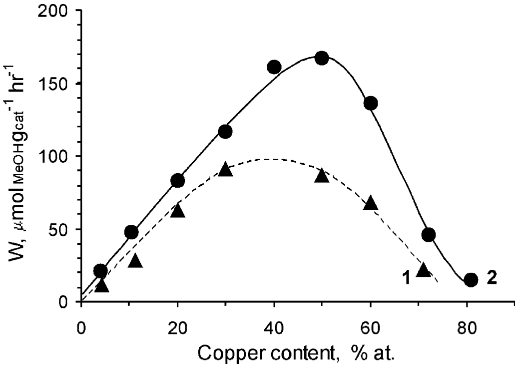

Fig. 1. The dependence of methanol synthesis catalytic activity of Cu-Zn catalysts on the copper loading (at.%); reaction conditions: at 493 K, 0.1 MPa, reaction gas composition H_2:CO:CO_2 = 15:4:1, methanol concentration 10^{-3} vol.%. 1, initial; 2, after operating 2 h at 623 K.

The nature of Cu^{2+} species stabilization in this structure still is not clear. Actually, Cu^{2+} can't settle to the regular ZnO structure, since occupying the octahedral positions there is forbidden, while tetrahedral coordination is unfavorable for Cu^{2+} cations. According to [5], the maximal concentration of Cu^{2+} in the "ideal" well-crystallized ZnO is less than 1 at.%. In

Table 1

Apparent coordination numbers (*N*), interatomic distances (*d*), Debye–Waller factors (σ^2) and energy shifts (E_0) obtained from fitting of the EXAFS data with *R*-factor (*R*)

	d (Å)	*N*	σ^2 (10^{-3} $Å^2$)	E_0 (eV)	*R* (%)
Uncertainity					
1st shell	±0.02	±10%	±20%		
Next shells	±0.04	±15%	±20%		
CuO					
Cu-O	1.96	3.9	5.5	0	
Cu-Cu	2.93	5.0	15.6	0	
Cu-Cu	3.09	4.0	11.5	13.3	
Cu-O	3.18	1.95	3.3	0	
CuZn					
Cu-O	1.94	3.8	6.0	−0.86	17
Cu-Zn	2.70	2.0	13.2	−22.8	
Cu-Cu	5.72	2.0	7.9	0.24	
CuZn-RO					
Cu-O	1.95	3.7	5.7	0.95	16.6
Cu-Cu	2.88	2.2	9.0	−6.1	
Cu-Cu	5.69	4.0	8.4	5.09	
CuZn-RORO					
Cu-O	1.94	4.2	5.9	0.011	19.2
Cu-Cu	2.88	1.0	3.1	−4.52	
Cu-Cu	5.70	4.6	8.1	9.27	
Cu^0 foil					
Cu-Cu	2.50	11.9	7.9	11.3	30.9
Cu-Cu	3.57	7.2	11.9	17.8	
Cu-Cu	4.36	20.6	10.3	9.2	
Cu-Cu	5.48	16.5	12.8	−20	
CuZn-R					
Cu-Cu	2.50	6.5	9.8	−2.83	25.0
Cu-Cu	3.54	3.0	14.7	−0.55	
Cu-Cu	4.38	10.8	13.9	−3.54	
Cu-Cu	5.44	4.4	6.6	−12.8	
Cu-O	1.94	0.5	14.9	−0.05	
CuZn-ROR					
Cu-Cu	2.52	6.4	13.2	0.07	31.8
Cu-Cu	3.54	3.6	11.4	−2.31	
Cu-Cu	4.41	12.0	19.3	0.2	
Cu-Cu	5.09	12.1	13.2	17.7	

In sample notations: *R* stands for reductive treatment in H_2 at 525 K, O stands for oxidative treatment in O_2–He mixture at 545 K.

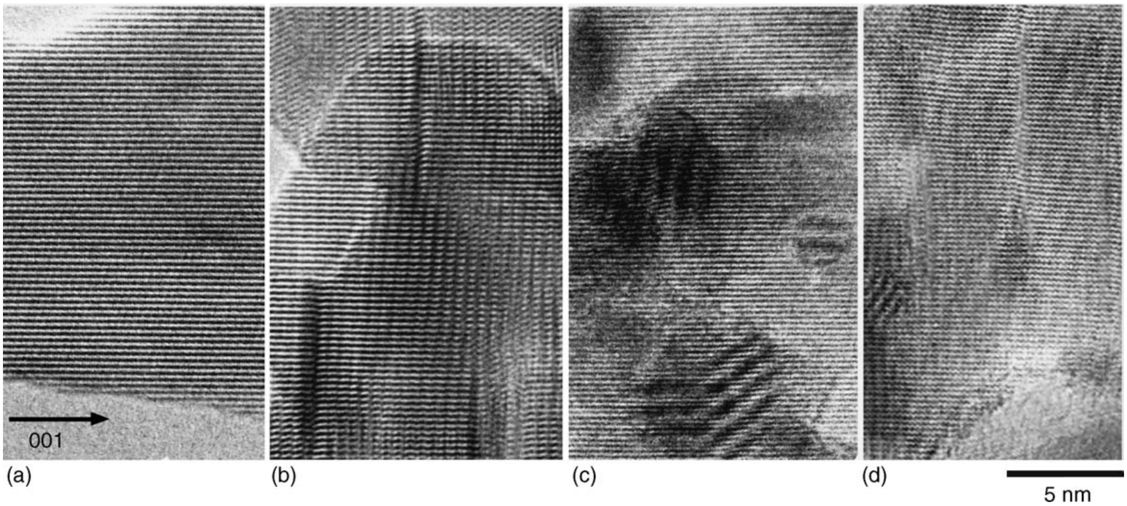

Fig. 2. HR TEM data of the 100% Zn sample calcined at 625 K (a), and 8%Cu 92%ZnO sample: calcined at 625 K (b), reduced in H_2 at 473 K (c) and reoxidized in O_2–He mixture at 525 K.

[6,7] it was supposed that the distortion of the ZnO structure due to the anionic admixtures of OH^- and/or CO_3^{2-} groups could help stabilizing Cu^{2+} cations in wurtzite-like structure. Calcination at temperatures above 800 K caused removal of anionic admixtures from the anion-modified wurtzite-structure, which is accompanied with the decomposition of the solid solution to individual oxide phases with ZnO and CuO structures. Below we will discuss a plausible nature of Cu^{2+} stabilization in the anion-modified zinc oxide using the model one-phase sample, which contains 8 at.% of copper.

3.2. The nature of Cu^{2+} stabilization in the anion-modified ZnO

The high-resolution TEM images are shown in Fig. 2 for the samples derived from co-precipitated Cu-Zn hydroxycarbonate with hydrozincite structure and Cu:Zn ratio of 8:92 in comparison to the 100% ZnO, derived from hydroxycarbonate (frame a). The initial calcined sample (frame b), the sample reduced in hydrogen at 475 K (frame c) and then reoxidized in in low concentration oxygen (0.05% O_2 in He) at 525 K (frame d). All the images are presented in the same scale and they are oriented with the (0 0 1) axes directed horizontally. The parameters of fitting Cu K-edge EXAFS are summarized in Table 1 for $Cu_{0.08}Zn_{0.92}O$ oxide sample (denoted as CuZn) as well as for this sample after its reduction in hydrogen (indexed with "R") and further re-oxidation in low concentration oxygen (0.05% O_2 in He, indexed with "O"). Detailed description of the Cu K EXAFS data will be published as a separate publication. More details on the HREM and XRD data for the samples under discussion could be found in recent publication [8].

Comparison of Fig. 2(a and b) shows unambiguously that the stabilization of copper cations in the ZnO structure is related with the high concentration of planar defects in the wurtzite-like structure. These planar defects are the stacking faults and missing planes in direction (0 0 1) of the hexagonal close packing of ZnO.

Data of Table 1 evidence that in the oxide CuZn sample the copper cations are localized in a distorted octahedral surrounding with the nearest Cu–O distance of 1.94 Å, they form ultra-small clusters comprising not more than 4 copper atoms. Distinguishing feature of this sample is interatomic distance at 2.70 Å, which should correspond to Cu–Cu or Cu–Zn distance at coordination number of ca. 2. Obviously, such copper site can't locate in the regular wurtzite-like structure. These data agree with the HREM observations that copper cations should be localized in the planar defects of the ZnO lattice. A plausible scheme of a copper site, which accords the EXAFS data is depicted in Fig. 3. There, the Cu^{2+} cation is

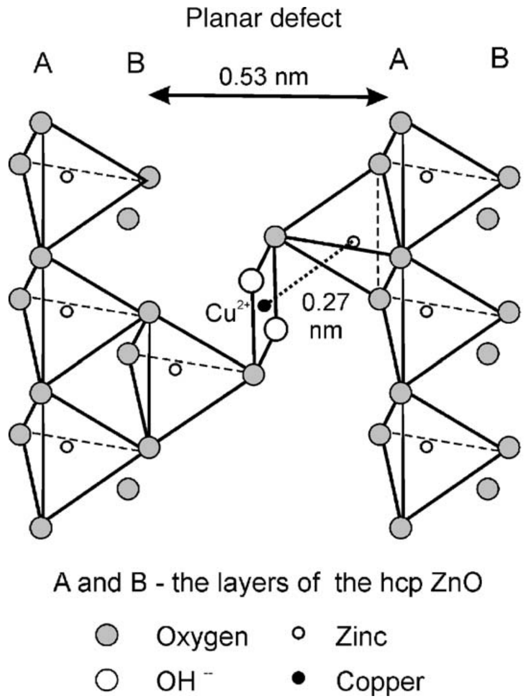

Fig. 3. Schematic presentation of the plausible environement of the Cu^{2+} cation stabilized in the planar defect of ZnO.

coordinated by two oxygen anions and two OH-groups and therefore could supposedly be described as the product of introducing (OH)–Cu–(OH) to an planar defect of the anion-modified ZnO. This scheme agrees to the earlier experimental data that anionic admixtures are crucial for the stabilization of Cu^{2+} cations in ZnO.

It is noteworthy that these data seem to give a bright example of the role, which could play the planar defects in stabilization of the alien cations in the oxide structure. This mechanism is close to that of ad-cation intercalation to the clay structures and could be common for low-temperature oxide structures. Note, that planar defects play a very similar role for stabilization of metastable non-stoichiometric alumina modifications [9].

3.3. Reversibility of the $Cu_{0.08}Zn_{0.92}O$ oxide reduction

Fig. 2(c and d) presents the data on the dynamic behaviour of the $Cu_{0.08}Zn_{0.92}O$ oxide under discussion when changing the medium to a reductive one and back to an oxidizing one. These data evidence that in H_2 at 475 K, most of Cu^{2+} cations leave the planar defects to form metallic particles with the diameter of 3–5 nm, which are epitaxially bound to the wurtzite structure (see Moire spots in Fig. 2(c)). The epitaxy of the metallic copper particles to ZnO structure is proved by electron diffraction data [8]. Well-expressed Moire interference may indicate small thickness of the flat metallic particles (ca. 2 nm). The data of EXAFS seem proving this supposition since the coordination numbers N_{Cu} in the reduced sample CuZnR are much less, than it could be expected for a spherical particle with diameter of 3–5 nm. Such low N_{Cu} should correspond to the flat particles with a thickness of ca. 4 periods of Cu^0 lattice, i.e. about 1.6 nm. Note that the formation of flat metallic copper particles over zinc oxide was previously deduced from low coordination numbers $N_{1Cu–Cu}$ by the authors of refs. [10,11]. In both cases, the sensitivity of metallic copper particles coordination to conditions of experiment has been found. The authors of the works cited supposed that the observed change in copper atoms coordination relates to the formation of flat and rather thin epitaxially bonded copper particles that reversibly change their shape to the spherical one with the reaction conditions.

Stacking faults are not visible in the HREM images of the sample treated in the reductive medium (H_2, 473 K), however they re-appear after the treatment in an oxidizing medium (0.05 vol.% of O_2 in He flow, 525 K), while metallic particles mostly disappear (Fig. 2(d)). EXAFS data evidence that the extended stripe-like clusters of Cu^{2+} cations in the flat square coordination appear during the re-oxidation in oxygen–helium mixture. The existence of Cu–Cu distance at 2.88 Å with coordination number $N_2 = 2.0$ and absence of any RDA maximum in the range of 3–5 Å can be reasonably attributed to a stripe-like chain of flat square coordinated Cu^{2+} cations in the ZnO planar defect. While repeating the reductive treatment (ROR) and once again re-oxidizing the sample (RORO) one observes the reversible transformation of the sample structure similar to the described above.

So, after being once reduced in H_2, the copper atoms form small Cu^0 particles, however they return to the planar defects of the ZnO structure as the extended stripe-like clusters after an oxidizing medium (0.05 vol.% O_2) is substituted for H_2. One hardly can suppose that a planar defect can be generated during the sample re-oxidation. Therefore, the observed reversibility indicates, that the planar defects are preserved during the reduction even despite copper atoms quit the planar defect. Definitely, the planar defect should loose its contrast in TEM image, after Cu^{2+} cations have left it. Therefore, one can resolve no extended defect of ZnO in Fig. 2(c).

4. Conclusion

The catalytic activity of CuZn catalysts in the synthesis of methanol seems to relate with those reduced Cu species, which originate from the $Cu_xZn_{1-x}O$ solid solution of wurtzite-like structure. Copper cations in the $Cu_xZn_{1-x}O$ solid solution are localized in the planar defects of the ZnO lattice. Copper sites could be supposedly described as the product of introducing $(OH)\cdots Cu\cdots(OH)$ to the planar defects of zinc oxide structure. Hydroxyl groups may stabilize the planar defects of ZnO. The process of the samples reduction leads to the Cu^0 state. The planar defects of ZnO structure are preserved even after reduction. During the reoxidation, copper atoms return back to the planar defects of ZnO as the clusters of flat-square coordinated copper cations. The clusters are ordered and have the stripe-like geometry. Reversibility of the reduction–reoxidation process evidence that the planar defects play important role for stabilization of the active Cu^0 particles.

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