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Localization of copper atoms in the structure of the ZnO catalyst for methanol synthesis

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The microstructure of a copper–zinc oxide catalyst for methanol synthesis has been studied using high resolution electron microscopy. Two alternatives for the arrangement of copper atoms in the zinc oxide crystallite were suggested and discussed. The high concentration of copper atoms in the sample (up to 10 atom%) against the known solubility of Cu^{2+} ions in ZnO (not more than 2 atom%), as well as the high density of dislocations seen in micrographs of the catalyst, may be accounted for by the occurrence of octahedral copper atom clusters of 0.25 nm radius built up into the host oxide lattice. These clusters lie at the dislocation wall along the (001) plane of ZnO. Copper atoms were also shown to be involved in isolated square planar CuO clusters not more than 0.5–1 nm in size.

Introduction

It is common knowledge that the most effective commercial process for methanol production is synthesis from H_2 and CO in the presence of copper–zinc–aluminium oxide catalysts. Characterization of these systems, especially under the reducing conditions of the catalytic process, is the objective of a number of researches.[1–6] These data indicate that Cu^+ and Cu^0 species appeared on the surface of the ZnO particles after catalyst reduction, and these species are believed to control the catalytic activity. At the same time, the localization of the copper atoms in the as-prepared catalyst is poorly understood. Studies show that copper may be dissolved in the ZnO lattice as Cu^+.[7,8] A cluster-like arrangement of copper atoms through the catalyst bulk has also been proposed, although this is not supported unambiguously by direct experimental evidence.[1,9] The aim of the present work was to study the microstructure of a model fresh copper–zinc oxide catalyst, and in particular, to investigate the possible cluster-like arrangement of copper atoms in the catalyst. High resolution electron microscopy was the main method of structural investigation.

Experimental

The catalyst sample was prepared *via* coprecipitation of a mixed solution of copper and zinc nitrates with a 10% aqueous solution of sodium carbonate at pH 7 and temperature of 70 °C. The deposits produced were washed to remove nitrate groups, then dried at room temperature and calcined at 350 °C for 4 h. The catalyst obtained had a nominal Cu : Zn atomic ratio of 10 : 90. The preparation procedure of pure ZnO was the same, but coprecipitation was performed with solutions of zinc nitrate and sodium carbonate.

X-Ray powder diffraction (XRD) was used to determine the phase composition of the samples. XRD patterns were recorded using a URD-6 diffractometer (Cu-Kα radiation, graphite monochromator at the reflected beam).

Experimental electron micrographs were recorded with a JEM-4000 transmission electron microscope (HRTEM) at 0.19 nm resolution. Elemental composition of the catalyst particles was determined using a Philips CM-200 transmission electron microscope fitted with an EDAX DX-4 microanalysis system with an energy-dispersive X-ray spectrometer (EDX). For the microscopic study samples were prepared by traditional methods: they were crushed in an ethanol slurry and the resulting solutions were dispersed on holey-carbon films supported on gold grids.

Theoretical HRTEM images were simulated to interpret the experimental micrographs. Modified software based on a multislice algorithm was used for the computation; the underlying principles of the algorithm are given in ref. 10. The computations were mainly accomplished for a cell of $5.6 \times 1.0 \times 1.3$ nm^3 consisting of more than 600 atoms.

Results and Discussion

XRD analysis revealed that the phase composition of the undoped oxide is pure ZnO (space group $P6_3mc$; a hexagonal cell; lattice constants $a = 0.324982$ nm, $c = 0.550661$ nm).[11] At the same time, only the peaks assigned to the zinc oxide phase were observed in the X-ray powder diffraction patterns of the catalyst.

According to TEM data, the parent ZnO particles are in the form of thin platelet crystals (*ca.* 10–15 nm in thickness, more than 0.1 μm in length) that correspond, as is evident from the selected area electron diffraction pattern [insert of Fig. 1(a)], to ZnO crystallites with (100) developed planes [Fig. 1(a)]. This is also confirmed by the results of the image simulation procedure. A simulated image of the structure of pure zinc oxide viewed along the [100] direction is situated at the bottom of Fig. 1(b), which shows a HRTEM image of pure ZnO. The light spots in this image are seen to correspond to close columns of Zn and O atoms along [100] and normal to the image plane. Catalyst particles are crystallized in the form of thin elongated platelets, similar to pure ZnO. There are no layers nor copper associates at the surface of the ZnO support [see Fig. 1(c)], but microanalysis data indicate the presence of copper in every catalyst particle. The copper content varies from 8.5–10.6 atom% from one crystallite to another. A typical EDX spectrum is shown in Fig. 1(d) (the Au-Lα and Au-Lβ peaks are due to the gold grid onto which the sample was placed).

By comparing HRTEM micrographs of pure ZnO and the copper doped catalyst [Fig. 1(b), (c)], one can see that catalyst particles possess a higher density of defects along the [100] direction than pure zinc oxide; there are a great number of edge dislocations and local variations of (001) lattice parameters in the case of copper doped ZnO. Besides, a non-uniform intensity distribution is observed in the image. At the same time, we do not see dislocations or any other distortions in the structure along the [001] crystallographic direction. Extra-

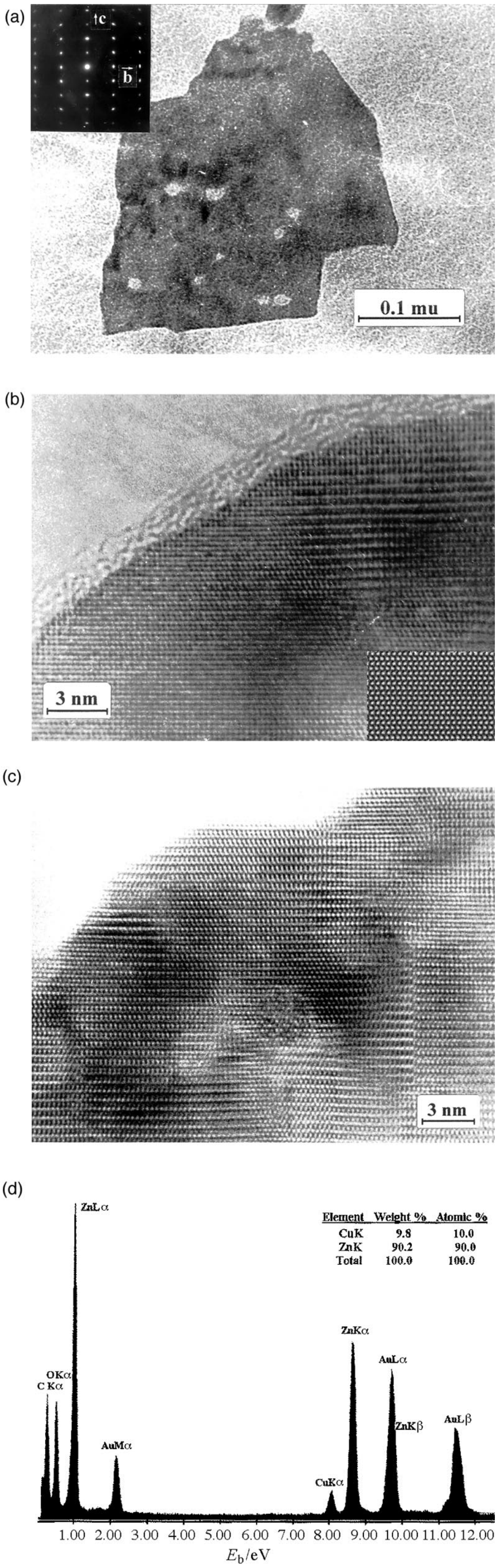

Fig. 1 TEM micrograph and selected area electron diffraction pattern of the (100) zone axis of pure ZnO (a) along with HRTEM experimental images of pure ZnO (b) and copper doped ZnO (c) oriented into the (100) projection; typical EDX spectrum obtained from an isolated catalyst particle (d)

bright spots and curved fringes observed in the micrograph of copper doped ZnO oriented into the [100] zone cannot be considered as an effect of electron beam damage during specimen examination in the microscope column, since we conducted our experiments at a working vacuum of 5×10^{-8} Pa at the specimen. Within this dry environment we did not observe any transformation of the sample structure, such as generation of point defects, dislocation loops or hole drilling, for at least 25 min. This time was long enough to examine the structure, to align a specimen into the proper crystallographic position and to take a picture. Therefore, taking into account the microanalysis data and the absence of the copper species on the surface of the host particles, it seems reasonable to assume that copper atoms are located within the bulk of the zinc oxide crystals in the vicinity of the numerous defects.

The observed defects are likely to be of a dislocation nature. If we assume that copper atoms are distributed statistically (or at random) through the ZnO crystal by incorporation into the positions of Zn atoms, then the theoretical images of such a structure coincide with the image of pure zinc oxide. This is quite plausible, since Zn and Cu atoms are almost equal to each other in scattering properties, hence the substitution of Cu for Zn does not affect the image contrast. Again, the model implying the solid solution does not explain the observed high concentration of copper in the sample; the limit solubility of copper ions in zinc oxide is *ca.* 2 atom%, whereas we observe 10 atom%.

It was proposed earlier[1,9] that copper atoms may form clusters in the structure of ZnO. This model is not contradictory to our experimental data and can be used to explain the high concentration of defects in the catalyst particles. For this reason, our further speculations will be based on this model. If we consider a cluster consisting of one copper atom with surrounding oxygen atoms in a distorted octahedral arrangement,[9] it is most probable that such a cluster occupies either the cation position, thus distorting the oxygen sublattice, or the sites between adjacent (001) planes that induce slight distortions to both anionic and cationic sublattices of ZnO. However, for both cases the HRTEM images of crystals with clusters of this type do not differ from the micrographs of pure ZnO.

We proposed alternative routes to cluster formation. Planar clusters composed of 2–4 copper atoms, which are fragments of the crystal cell of CuO, were considered. For example, the atoms of the clusters based on 2 copper atoms are arranged at the opposite corners of a parallelogram, and oxygen atoms occupy the neighbouring corners. Geometrically, such clusters can be easily incorporated into the (001) cationic plane of ZnO at Zn atom positions, and oxygen atoms are situated in the adjacent anion planes [Fig. 2(a)]. Relaxation is achieved with disturbance of the oxygen sublattice, and there is a small defect range. Therefore, there is no distortion in the computed HRTEM images. If we consider a group of such planar clusters, or clusters of larger size, then they tend, while relaxing, to move oxygen atoms along the [100] or [010] crystallographic directions at the (001) anion plane of ZnO, which gives rise inevitably to the appearance of the dislocation loop. A theoretical image computed for the dislocation loop with CuO clusters is shown in Fig. 2(b). However, comparing the simulated image with experimental micrographs, one can see that they do not fit well. Our calculations revealed that at a CuO cluster concentration not higher than 2 atom% they do not induce such distortions as dislocation loops in the structure of ZnO. Therefore, only small numbers (*e.g.*, 2 atom%) of CuO type clusters might exist in the sample. However, remember that, according to EDX data the concentration of copper atoms in the catalyst particles is much more higher, over 10 atom%. Hence, the model involving only CuO clusters cannot be used to explain the high content of copper atoms and defects in the sample.

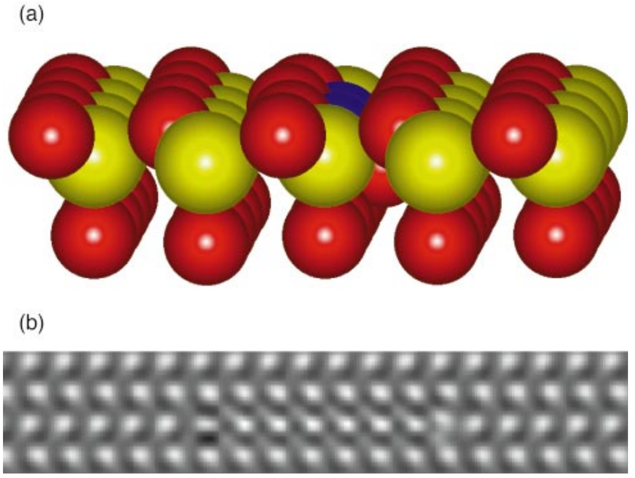

Fig. 2 Schematic representation of the location of the CuO cluster in the (100) plane of the ZnO structure (a) and its HRTEM simulated image (b). Oxygen, zinc and copper atoms are shown as red, yellow and blue balls, respectively.

These speculations lead us to the suggestion that copper atoms may be arranged as 'bulky' clusters in the zinc oxide crystals. Analysis of the micrographs indicates that defects occurring in the structure of the catalyst particles are rather local. As they are no more than a few nanometers long, they remain confined to the two (001) adjacent planes. The defects may be either dislocation loops or dislocation walls. As mentioned above, the situation of the dislocation loop was not reliable, so the model based on a dislocation wall of 1–2 nm in size was considered. The presence of a copper atom cluster of 0.25 nm radius in this cavity may stabilize such a defect configuration. The most stable clusters of copper atoms are known to be those involving 15, 18, 19, or 20 atoms.[12] It is most probable that a 0.25 nm cluster comprises 19 copper atoms. According to computations cited in ref. 13, such a cluster should be octahedral with an atom in the center [Fig. 3(a)] which would allow the highest stability. This octahedral cluster was used as a model for further consideration.

Before analyzing the effect of such a cluster on the HRTEM image of the catalyst, let us describe in detail features of its incorporation into the bulk structure of ZnO. It seems likely that the cluster is arranged in the bulk of a ZnO microcrystal in such a manner that its central plane (six Cu atoms in the corners and one in the center of the right hexagon, seven atoms in total) lies at the (001) plane of the cationic sublattice of ZnO to form vacancies at the positions of seven Zn atoms; copper atoms are incorporated into these vacancies. It is possible here that the oxygen atoms in the neighbouring anionic planes retain their positions but are slightly shifted. Fig. 3(b) gives a probable arrangement of copper atoms at the (001) plane of ZnO. This atomic plane with copper atoms incorporated in it will be hereafter considered as the basis and referred to as the central atomic plane. Two neighbouring planes will be called the upper and lower planes, respectively. There are six copper atoms in each of the upper and lower planes. These atoms are arranged in the corners and at the edge centers of an equilateral triangle. In this case, the lower atomic plane of zinc oxide is not shifted, since vacancies at the positions of six zinc atoms allow the incorporation of the cluster plane in the same manner as occurs in the central atomic plane, when copper atoms occupy the zinc vacancies. Such an arrangement is also attributed to the close positions of copper and zinc atoms in the planes. There is a somewhat different configuration at the upper cationic plane of ZnO: copper atoms lie in between zinc atoms. For this reason 12 Zn vacancies and, additionally, displacement of oxygen atoms by a half period around the cluster are needed for the incorporation. Therefore, Zn and O atoms are most likely to be shifted along the [001] direction by a quarter of the interlayer distance; there is no need for Zn or O vacancies in this case. Eventually, a dislocation wall of *ca.* 0.5 nm height and 0.6 nm radius is formed at the (001) plane of ZnO. A diagram of the cluster arrangement along the [100] direction is shown in Fig. 3(c), the upper layers of ZnO are not depicted for simplicity. The relaxation of the whole system is attained through the oxygen sublattice of ZnO, to which the cluster is likely to be bound. Such a dislocation can be treated as two sequential opposite edge dislocations, which cannot merge because of the cluster between them.

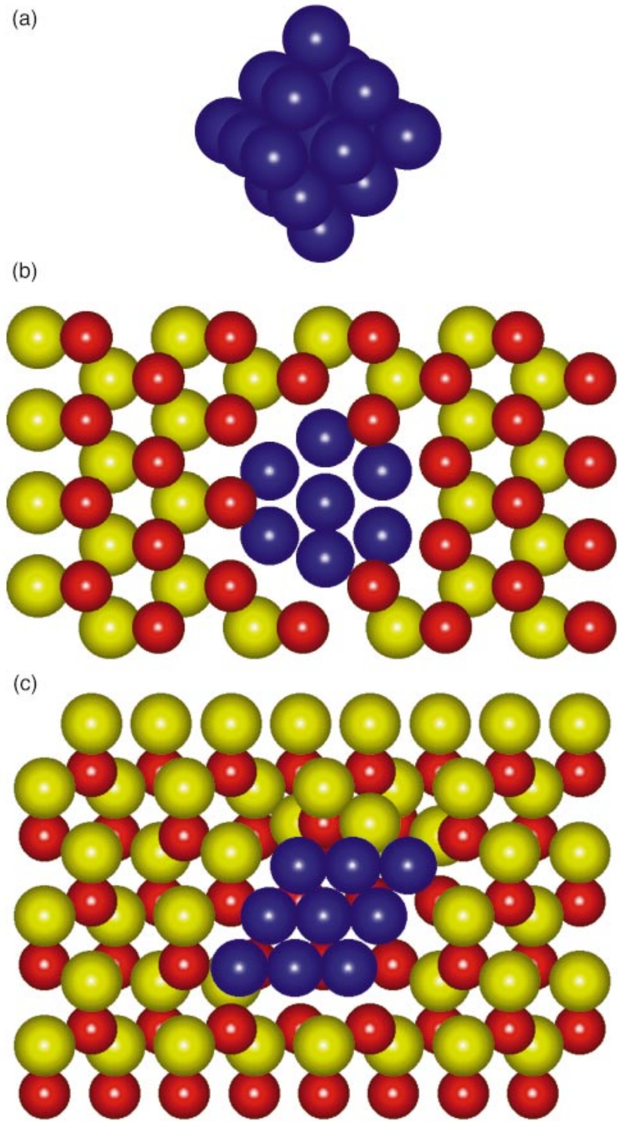

Fig. 3 Configuration of the octahedral copper atomic cluster (a) and its location in the (001) (b) and (100) (c) planes of the ZnO structure. Atom colours as in Fig. 2.

A theoretical HRTEM image of a crystal with such a cluster is shown in Fig. 4, no. 2 (image 1 is the theoretical image of pure zinc oxide). Minor changes are seen in image 2. First, the spot glow becomes more intense at the point where the center of the cluster is situated. This phenomenon is caused by the presence of copper atoms, or more precisely, by the presence of a denser group of copper atoms in the column of zinc atoms corresponding to this spot. We emphasize that exchange of copper atoms for zinc in the regular positions of the cationic sublattice of zinc oxide does not have any effect on the spot brightness in the simulated image. However, incorporation of the copper atom cluster into the ZnO structure leads to a

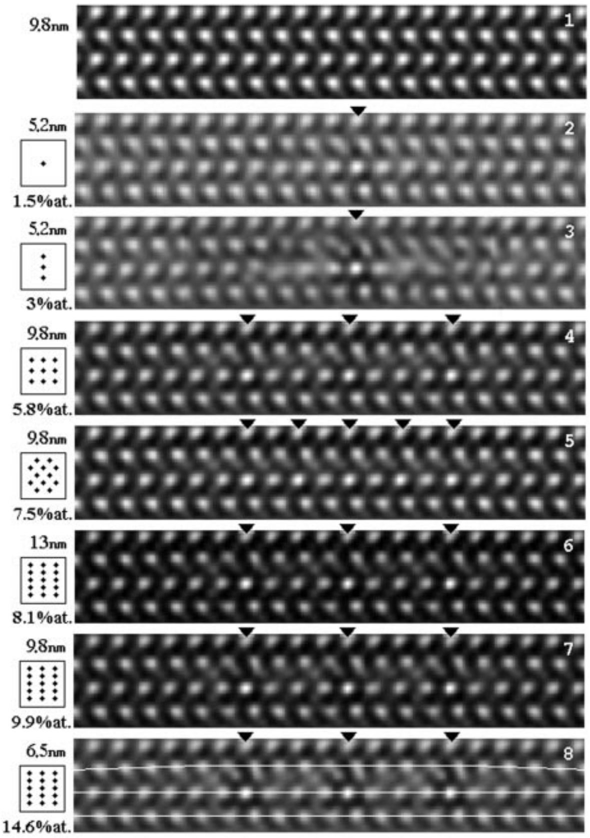

Fig. 4 Sequence of HRTEM simulated images of the ZnO structure oriented into the [100] zone axis with different copper cluster contents in the oxide structure

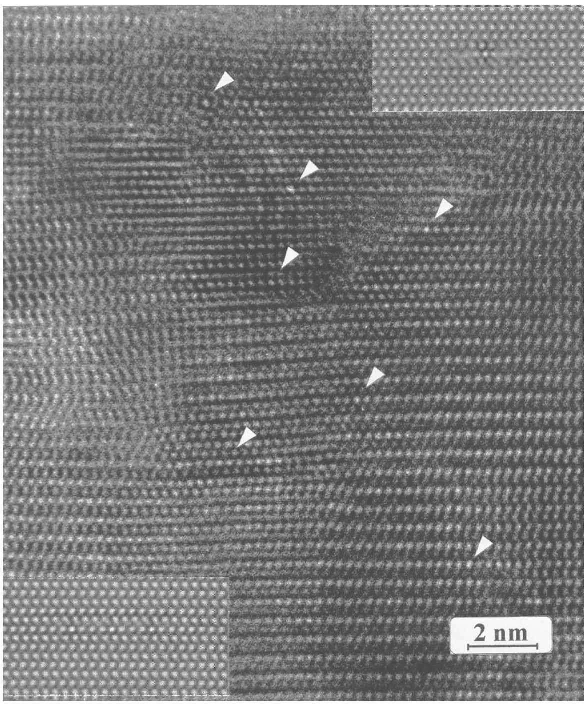

Fig. 5 HRTEM experimental image of the copper doped ZnO particle structure viewed along the [100] direction with simulated images of the one (the right top corner) and nine (the left bottom corner) octahedral clusters built up in the structure of the host crystallite. Some interesting features in the experimental image are arrowed (see details in the text).

change of the period in the column, which gives rise to the variation in contrast. There is evidence for contrast weakening at the row interstices: two spots from neighbouring atomic rows transform into a single diffuse strip. In fact, this is a result of electron beam scattering by the defect. The experimental micrographs show such individual bright spots to appear rather frequently, the same smearing as in the theoretical images being observed. Eventually, we can see that the simulated image is identical to the experimental one, although the copper concentration is still low (1.5%) in this case.

At the same time, several clusters may house a cavity to provide a different concentration of copper atoms in the ZnO structure. Computed HRTEM images for alternative arrangements of clusters in cavities are shown in Fig. 4 (diagrams of cluster arrangements in cavities are shown on the left). Unlike the images of undoped zinc oxide, the intensity distribution changes: a portion of spots assigned to the positions of the clusters is brighter, and the other spots darker. The spot contrast seems to be in direct proportion to the concentration of copper atoms in the column. By introducing clusters into the structure of the oxide crystal, we have been able to obtain a very slight bending of the atomic row in the simulated image since the value of the shift of the upper atomic plane along [001] during the cluster incorporation was very small (about 0.05 nm). This bending is depicted by bold lines in the simulated image shown in Fig. 4 (no. 8). But when the crystal thickness increases, bending of the fringes becomes practically invisible in the calculated pictures.

Let us compare the model images with the experimental micrograph which is shown in Fig. 5. For convenience, simulated images of the two configurations involving one and nine clusters in the cavity are inserted at the top right and bottom left of this figure, respectively. Row curving is often observed in the experimental micrographs (arrowed in Fig. 5). Typically, this occurs as a single curved row surrounded by straight rows. But there is only half-noticeable curving of the atomic fringes in the model images. Strong curving of the atomic rows, visible on the micrograph, is believed to be a result of the presence of more than two dislocation walls closely spaced in the structure of ZnO. In this case one may expect the same pronounced bending of rows, similar to the edge dislocation. However, we could not perform a simulation using this model due to its complexity and the great number of atoms involved into the calculation.

An increase in the brightness of the spot assigned to the cluster center is seen in the region of the cluster location in the structure of ZnO in the model images (Fig. 4, nos. 2 and 3). Similar enhanced brightness of isolated spots in the row often occurs in the micrographs (Fig. 5, arrowed) which indicates, according to the simulation results, the presence of one or several clusters in the ZnO structure. Calculations revealed also that at sufficient crystal thickness (see Fig. 4, no. 6) the distortion of the atomic rows induced by the dislocation becomes less pronounced whereas the brightness of the spot assigned to the cluster center still remains anomalous. The same is seen in the HRTEM micrographs. Earlier Suzuki and Takeuchi[14] studied defects in pure ZnO and observed a similar bending of the atomic rows, but did not report on the nonuniform intensity distribution in the image in the defect regions. An experimental HRTEM micrograph of our undoped ZnO also provides evidence for the absence of extrabright spots [see Fig. 1(b)]. Thus, these facts may be considered as additional arguments for the possible arrangement of copper atoms as octahedral clusters in the bulk ZnO structure.

It should be noted that, according to our model, only slight variations in the image are expected in the [001] direction, which is normal to the [100] direction we considered above. This is because Zn and O atoms are mainly shifted along the [001] direction when the cavity is formed. Therefore, variations in the spot brightness around the dislocation wall and, probably, a slight variation in the contrast at the inter-row gap at the cluster localization sites may be the most visible effects on

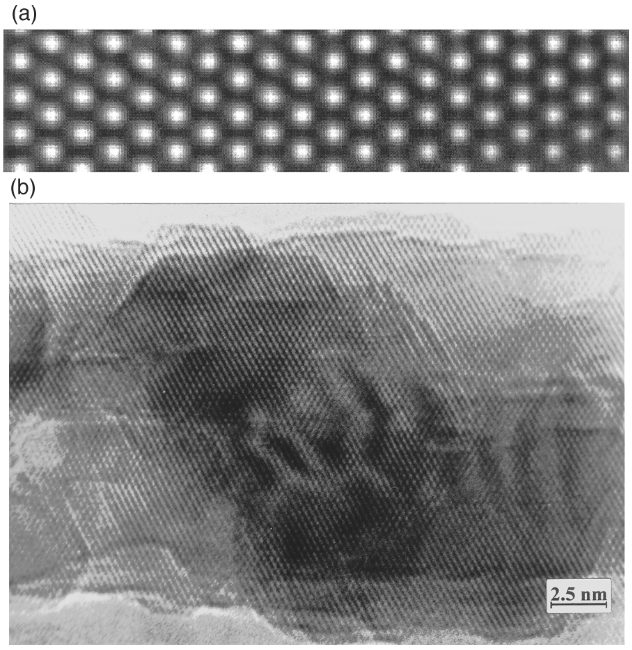

Fig. 6 HRTEM simulated (a) and experimental (b) images of the structure of the copper doped ZnO microcrystal viewed along the [001] axis

the image. However, these effects are so weak that no distortion along the [001] direction is observed in the computed images [Fig. 6(a)]. Indeed, the experimental micrographs do not show considerable changes along this direction, namely, extrabright spots or row bending [Fig. 6(b)]. The atomic fringes in the copper-doped ZnO are seen to be arranged in the same fashion as those in the undoped ZnO, except for weak concentric rings, which may be the results of microstrains arising in the structure due to the presence of copper clusters in the bulk of the ZnO crystallite.

Along with HRTEM images, an electron beam diffraction pattern was computed based on the model crystal image. There was no extra reflection in the diffraction pattern, but a slight variation in the brightness of reflections, assigned to the pure zinc oxide, was observed. Such a pattern fits well with the XRD data. Being small in size, defects in ZnO particles do not cause global structural transformations and, hence, do not give rise to additional diffraction spots.

Undoubtedly, features of the preparation procedure strongly affect the specific microstructural organisation of the catalyst. Thus, some authors[15] used the same solution of copper and zinc nitrates as we used, for coprecipitation but calcined the catalyst at a higher temperature (450 instead of 350 °C) for 8 h longer than in our system. As a result, they obtained a catalyst with highly dispersed fine crystallites of CuO supported on ZnO. For our sample, low temperature calcination for a relatively short time (4 h) seems to favour trapping of the copper atoms inside the structure of zinc oxide instead of their migrating onto the surface of ZnO particles. Owing to these mild preparation conditions, residual CO_3^{2-} groups which result from incomplete thermal decomposition of the aurichalcite precursor, $(Cu,Zn)_5(CO_3)_2(OH)_6$, have been detected in the catalyst structure.[16] The presence of these groups can also contribute to stabilization of both the cluster and the cavity in the bulk of the ZnO particle.

A rather intriguing problem is the stability of such a system. The electronic structure of these clusters is not clearly understood, especially with regard to the fact that the cluster is not at the surface but in the bulk of the ZnO crystal. However, if we consider a free cluster composed of one sort of atom (copper atoms in this case) then the optimal shape is an octahedron of 0.256 nm radius. The Cu_{19} cluster corresponds to a 'magic' number and is known to be stable enough.[12,13] Compressing forces generated by the curved (001) plane of ZnO affect the incorporated cluster. However, there is only a slight shift (0.054 nm) of the plane from the equilibrium position. Hence, these forces must be comparable with the forces operating in the cluster, which results in the stability of the whole system. The cluster itself undergoes a slight deformation $[(10\text{–}20)\times10^{-12}\ \mathrm{m})]$. On the other hand, the cluster might be bonded to the oxygen sublattice of the crystal which would contribute to its stability. The latter case can be regarded as the formation of a bulky octahedral Cu—O cluster which is strongly linked to the zinc oxide lattice. We can only guess which of these two arrangements is most reliable. Knowledge of, at least, the nature of the bonds in the cluster is needed to support either suggestion, but this falls beyond the scope of the HRTEM method.

Our model implies the occurrence of an extended dislocation wall producing a cavity that might facilitate the migration of copper atoms towards the crystal surface during the specimen treatment in the reaction mixture. The study of the change of the catalyst microstructure in the reducing atmosphere will be the subject of a forthcoming publication.

Conclusions

The structure of a copper–zinc oxide catalyst was studied using the HRTEM technique. Several alternative arrangements of copper atoms in the structure of the zinc oxide crystal were considered. Model images of such systems were computed and compared to the experimental micrographs. The studies showed a number of defects in the ZnO matrix. The defects are the result of incorporation of copper atoms into the ZnO structure, copper atoms being arranged as octahedral clusters, stabilized by residual carbonate groups. Additionally, isolated small (*ca.* 0.5–1 nm) distorted square-planar CuO clusters may occur.

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