



HRTEM study of Cu/ZrO₂ catalyst. An evidence of a new perovskite-like oxide ZrCuO₃

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Copper based catalysts can be used for reactions such as water-gas shift, methanol synthesis, and methanol steam reforming. Some investigations have been done recently on catalysts containing both copper and ZrO₂ (zirconia) with respect to above reactions. In this context, zirconia may be either used as stabilizing additive to Cu/ZnO(Al₂O₃) catalysts [1], or as alternative support replacing e.g. ZnO [2]. Zirconia modified with anions such as sulphate is an acid catalyst and became known for its extraordinary activity in low-temperature alkane isomerization [3]; it is also active for a number of other acid-catalysed reactions [4].

In this work the high-resolution transmission electron microscopy (HRTEM) was used to characterise a Cu/ZrO₂ catalyst. The detailed results of the study will be published elsewhere; in this paper an evidence of the formation of a new perovskite-like oxide is reported.

A templating procedure [5] was applied for the synthesis of the CuO/ZrO₂ material, which involved the use of an acrylamide/glycidyl methacrylate polymer gel template [6] formed in an aqueous Tween-60 (Aldrich) solution at 55 °C. After cleaning and solvent exchange to n-propanol the gel was soaked in a zirconium (IV) propoxide (Aldrich, 70 % by mass in n-propanol) solution containing copper(II) acetylacetonate (Aldrich, 2.0 g) for 16 h to give theoretically

an 11 % Cu to Cu+Zr mass ratio. The impregnated gel was then placed into a mixture of n-propanol/water (1:1 v/v) and left overnight during which hydrolysis reactions occurred. The hybrid material was dried at room temperature open to the atmosphere, and then calcined at 450 °C (ramp 215 °C·h⁻¹) under a nitrogen then oxygen atmosphere to remove the organic material. The resulting powder was kept for 10 h at 250 °C under 1 atm pressure in a helium atmosphere containing 2 % of hydrogen that caused complete reduction of Cu, as found with in-situ X-ray powder diffraction (XRD) and X-ray absorption spectroscopy (XAS). With an XRD profile fitting procedure performed with the RIETICA software (Howard & Hunter, 1997) using the Pseudo-Voigt peak shape function and structural models taken from the ICSD database (FIZ Karlsruhe, Germany) the content of metallic Cu was estimated as 8 wt %, while the X-ray microanalysis showed the overall Cu content of 11 wt %.

The sample was dispersed in acetone, sonicated for 10 min. and deposited on a Ni grid covered with a 5 nm thick amorphous carbon film. A Philips CM200FEG transmission electron microscope was used for the material characterization. HRTEM images with a pixel size of 0.044 nm were taken at the magnification of 1083000× with a CCD camera and Fourier-transformed to obtain the power spectra (PS), which were used for measuring interplanar distances

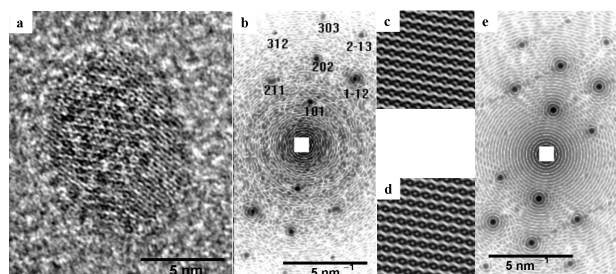


Fig. 1. a) HRTEM image of the ZrCuO_{3-d} nanoparticle; b) power spectrum of the image in a); c) Fourier-filtered (reconstructed) image; d) simulated image; e) power spectrum of the simulated image.

and angles within the accuracy of $\pm 1\%$ and ± 0.5 deg, respectively. The observed patterns were compared to those calculated from the crystal structures stored in the ICSD. The accuracy was sufficient to identify the crystalline phases unambiguously in most cases when the orientation of crystal lattice with respect to the electron beam allowed a certain set of d-spacings and angles to be measured.

TEM study has shown that the sample consisted of nanoparticles (4-15 nm) of tetragonal (*t*) and monoclinic (*m*) polymorphs of ZrO₂ (40 % and 60 % with the mean particle size of 7.4 nm and 9.2 nm, respectively), CuO (6 %), Cu₂O (6 %), and metallic Cu (88 %). A few particles of Cu₄O₃ were also found. The various copper oxides probably were formed due to the short exposure to air during sample transfer. It should be noted that the observed amount of *m*-ZrO₂ is in conflict with parallel XRD investigations, which indicate a *m*-ZrO₂ content of $\leq 10\%$. Having checked that the sample pre-treatment for the TEM experiment (sonication) did not change the XRD pattern, we suspect that the thermovacuum conditions (pressure of $2.5 \cdot 10^{-5}$ Pa and temperature of $n \cdot 10^2$ °C) inside the column of the electron microscope are responsible for the observed discrepancy in the ZrO₂ phase ratio. A hypothetical mechanism could involve desorption of certain species from the surface of the zirconia which had stabilized the tetragonal polymorph of ZrO₂ at ambient conditions [7]. The removal of these adsorbates may have changed the surface energy of the particles, resulting in a *t* \rightarrow *m* phase transition for part of the material. The beam-induced heat alone cannot easily account for this *t*-ZrO₂ \rightarrow *m*-ZrO₂ conversion, since the opposite case of an *m* \rightarrow *t* phase transition under the electron beam was observed in situ in isolated ZrO₂ nanoparticles (to be published elsewhere).

A few particles were found that could not be identified as those of the known oxides of Cu or Zr nor of the other phases. An HRTEM image of one of them is shown in fig. 1a. It was hypothesized that the particles represent the mixed oxide CuO-ZrO₂ = ZrCuO_{3-d} with, presumably, a perovskite or perovskite-like structure (the quantity of d, the oxygen deficiency normally found in perovskites, was unknown in our work). Fig. 1b shows the PS of the image indexed according to this supposition for the [111] viewing direction. The reconstructed image obtained by an inverse Fourier transformation after the background subtraction and

central spot removal from the PS is shown in fig. 1c. The unit cell parameters of an orthorhombic lattice calculated with a least-squares procedure using the following set of interplanar distances $d_{011} = 0.482$ nm, $d_{101} = 0.426$ nm, $d_{121} = 0.298$ nm, $d_{112} = 0.249$ nm, $d_{022} = 0.241$ nm, $d_{202} = 0.213$ nm, $d_{123} = 0.169$ nm, $d_{033} = 0.161$ nm, $d_{213} = 0.160$ nm, $d_{134} = 0.127$ nm, $d_{224} = 0.125$ nm were $a = 0.618 \pm 0.006$ nm; $b = 0.845 \pm 0.009$ nm; $c = 0.584 \pm 0.003$ nm.

Figure 1d shows the best result of the HRTEM image contrast simulation performed with the EMS software using the Bloch waves calculation algorithm [8]. For the simulation the cell parameters above and the fractional atomic coordinates of the distorted perovskite structure of NdCuO_{2.93} [9] were used assuming the Zr ions to occupy the positions of Nd. The structures of other perovskite-like compounds with the common formula ABO₃ and with A = Zr, B = Cu as well as with A = Cu and B = Zr were also tested, but the simulated images did not fit the experimental one. For easier comparison the PS of the simulated image is shown in fig. 1e.

The results presented provide a strong indication on the possible formation of the ZrCuO_{3-d} phase with a distorted perovskite GdFeO₃-type structure [10] in nanocrystalline form.

It was shown that a pressure up to 10 GPa was necessary to synthesize the perovskite-like cuprates of rare earth elements like NdCuO_{3-d} [9]. For the appearance of a similar phase of ZrCuO_{3-d} in our experiments an explanation based on increased effective internal pressure due to surface curvature and small particle radius (the Gibbs-Thomson effect) may be proposed. The difference between external and internal pressure Δp is known to be proportional to the surface energy γ and to the inverse of the particle radius r : $\Delta p = 2\gamma/r$. Winterer et al. [11] have estimated the value of $\Delta p = 3$ GPa for 8 nm particles of ZrO₂. The surface energy of the new ZrCuO_{3-d} phase is unknown, but it may be assumed that the value is of the same order as that of zirconia. With nearly the same particle size (fig. 1a) as in the above mentioned estimation the internal pressure in the nanoparticles studied in this work might be quite comparable to that used in [9].

On the other hand, the phases of LnCuO_{3-d} with Ln = Y, Sm, Gd have not been synthesized at the same pressure due to, as suggested in [9], small size of these cations, which prevented them from being stabilized in eight-coordinated site of cuprite perovskite. Zr cation is even smaller than those listed. The concept of the increased pressure alone cannot explain the stability of ZrCuO_{3-d}.

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