

New Highly Mixed Phases in Ball-Milled Cu/ZnO Catalysts as Established by EXAFS and XANES

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Abstract. AnXAFS investigation at both the Cu and Zn K-edge has allowed to unravel new highly mixed phases in Cu/ZnO catalysts prepared by ball-milling mixtures of Cu₂O and ZnO under 3 different atmospheres of synthetic air (SA), SA+CO₂ and CO₂. The system milled in CO₂ shows the disproportionation of Cu₂O into Cu⁰, Cu¹⁺ (cuprite Cu₂O-type phase) and Cu²⁺ (tenorite CuO-type phase), while most of the Zn²⁺ is transformed into a nanocrystalline / amorphous ZnO-type zincite that forms a superficial mixture of oxide and carbonate phases. When synthetic air is added to the CO₂ atmosphere, ball-milling results in the oxidation of part of the Cu¹⁺ into Cu²⁺ with no Cu metal formed. In SA, a significant amount of Cu²⁺- and Zn²⁺-based phases react to form a nanocrystalline / amorphous Cu_{1-x}Zn_xO solid solution that was never reported before. This distorted rock salt-like solid solution, in which Zn and Cu feature different octahedral environments, is formed by incorporation of Zn²⁺ in the Cu₂O matrix and the concomitant oxidation of Cu¹⁺ into Cu²⁺ and results from strong Cu/Zn interactions in the Cu/ZnO system.

Keywords: EXAFS, XANES, HRTEM, Catalysis, Copper, Zinc.

PACS: 61.10.Ht X-ray absorption spectroscopy: EXAFS, NEXAFS, XANES, etc.; 68.37.Lp Transmission electron microscopy (TEM) (including STEM, HRTEM, etc.); 61.43.-j Disordered solids; 82.45.Jn Surface structure, reactivity and catalysis.

INTRODUCTION

Cu/ZnO catalysts are widely used in industry for (de)hydrogenation of organic functional groups. A high activity is generally obtained when an intimate mixture of Cu and ZnO is achieved, but despite decades of research, controversy still exists about the nature of the active site. As an alternative to the usual coprecipitation methods used to prepare highly mixed catalyst systems, a mechanochemical method can be applied that additionally allows solid-state reactions between the individual particles as well as reactions with the gas atmosphere. Consequently, by ball milling of Cu_x/ZnO mixtures, intimately mixed precursors may be produced for the highly active methanol synthesis catalyst [1,2]. In order to unravel the complex structures of a series of systems obtained after ball milling Cu₂O/ZnO in different atmospheres, a XAFS investigation has been carried out at both the Cu and Zn K-edge.

EXPERIMENTAL

Three different materials have been prepared by ball milling cuprite Cu₂O and zincite ZnO mixtures (Cu:Zn atomic ratio 30:70) in synthetic air (BM_{SA}), synthetic air plus CO₂ (BM_{SA+CO2}), and pure CO₂ (BM_{CO2}). Typically 2 g of a mixture of Cu₂O and ZnO was milled during 200 h under 2 bar in a vibratory mill. High Resolution TEM was performed on a Philips CM30UT electron microscope operated at 300 kV. XRD patterns were recorded with an Enraf Nonius CPS-120 diffractometer using Cu-K α radiation. X-ray absorption data were collected on DUBBLE at ESRF (Grenoble, France) operating at 6 GeV, 200 mA using a Si (111) double-crystal monochromator. XAS signals were measured in transmission mode both at Cu and Zn K-edges. Data reduction and EXAFS refinements (k^3 weighting) were performed using respectively the programs EXBROOK and EXCURV98. Phase shifts and backscattering factors were calculated ab initio using Hedin-Lundqvist potentials.

RESULTS AND DISCUSSION

XRD and HRTEM

Figure 1 presents the HRTEM images of the ball-milled materials, whereas Figure 2 shows their corresponding XRD patterns. TEM measurements

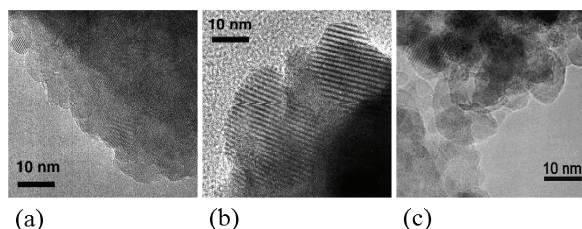


FIGURE 1. HTREM images of ball-milled materials a: BM_{SA}; b: BM_{SA+CO2}; c: BM_{CO2}

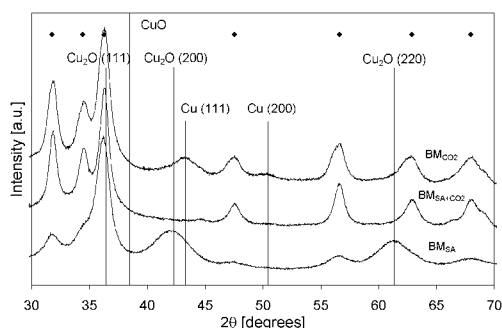


FIGURE 2. XRD patterns of ball-milled materials; ZnO peaks are represented by diamonds.

show that all materials have a nanocrystalline character (crystallites sizes of 3 to 20 nm) and a relatively similar morphology. The XRD patterns of BM_{CO2} and BM_{SA+CO2} show broad reflections belonging to the ZnO phase. No clear Cu₂O or CuO peaks can be detected, which indicates that Cu is present in either amorphous or nanocrystalline phases. Interestingly, XRD shows that a significant amount of Cu⁰ is present in BM_{CO2}. BM_{SA} pattern presents two intense and broad diffraction peaks, corresponding apparently to a nanocrystalline Cu₂O phase. However, this is in contradiction with previous TPR measurements [2] that pointed towards nearly complete oxidation of copper into Cu²⁺. These two reflections may not belong to the Cu₂O phase, but to another phase resulting from a strong Cu/Zn interaction.

XANES

Figure 3 shows that the XANES spectra at Cu K-edge of the three ball-milled materials are all very dif-

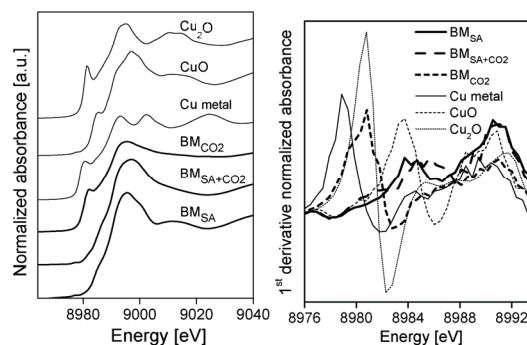


FIGURE 3. Cu K-edge background subtracted and normalized XANES spectra (left) and first derivatives (right) of the three ball-milled materials and bulk reference samples.

ferent in terms of edge position, white line intensity and shape of the resonance peaks after the edge. Comparison of the first derivatives shows that BM_{SA} curve is very similar to that of bulk CuO suggesting that the Cu phase in this material is mainly composed of Cu²⁺. In BM_{SA+CO2}, the small bump at 8980.3 eV corresponds to a strong feature in bulk Cu₂O, indicating that in addition to Cu²⁺ a substantial amount of Cu¹⁺ is present in this sample. Finally, BM_{CO2} shows a main peak located at lower energies that is apparently a combination of the main features of Cu metal and Cu₂O references.

EXAFS

Phase-corrected FT's of the EXAFS of the three samples at the Cu and Zn K-edges are given in Figure 4. A clear difference can be observed between the 3 materials especially at the Cu K-edge. Results of the EXAFS fits are summarized in Tables 1 and 2 for Cu and Zn K-edges, respectively. At the Cu K-edge, the first

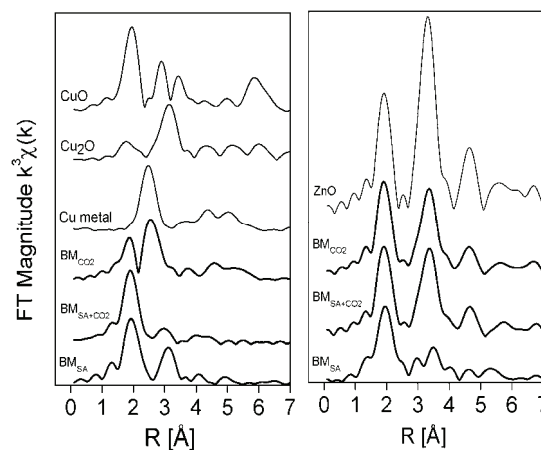


FIGURE 4. Phase-corrected Fourier transforms at Cu K-edge (left) and Zn K-edge (right) k^3 -weighted EXAFS of ball-milled materials and bulk references.

TABLE 1. Results of the EXAFS analysis at the Cu K-edge for the three catalysts for 3 selected N_i shells.

Materials	N_1	R (Å)	$2\sigma^2$ (Å ²)	N_{2+3}	R (Å)	$2\sigma^2$ (Å ²)
BM _{SA}	3.8 O	1.95	0.017	6.6 Zn	2.94	0.04
BM _{SA+CO2}	3.5 O	1.93	0.015	1.0 Cu	2.83	0.03
				1.2 Cu	3.79	0.03
BM _{CO2}	2.0 O	1.91	0.016	1.8 Cu	2.55	0.01
				0.7 Cu	3.02	0.02

TABLE 2. Results of the EXAFS analysis at the Zn K-edge for the three catalysts for 3 selected N_i shells.

Materials	N_1	R (Å)	$2\sigma^2$ (Å ²)	N_{2+3}	R (Å)	$2\sigma^2$ (Å ²)
BM _{SA}	4.4 O	1.98	0.022	2.4 Cu	2.97	0.02
				3.4 Zn	3.16	0.02
BM _{SA+CO2}	3.7 O	1.96	0.015	1.2 C	3.06	-
				4.1 Zn	3.21	0.02
BM _{CO2}	3.6 O	1.96	0.015	1.4 C	3.06	-
				4.6 Zn	3.20	0.01

peak in both BM_{SA} and BM_{SA+CO2} corresponds to 3.6 O and only 2 O in BM_{CO2}. Cu-O bond distance, which varies from 1.95 Å in BM_{SA} to 1.91 Å in BM_{CO2}, shows a constant decrease when the amount of SA in the mill vial is reduced. These distances correspond either to the Cu-O bond distance in tenorite (1.95 Å) or to an average distance in a mixture of tenorite and cuprite phases that features a shorter Cu-O bond distance (1.85 Å). In BM_{SA+CO2}, Cu-Cu bond distances correspond roughly to the typical Cu-Cu distances in CuO (2.90 and 3.74 Å). In BM_{SA}, the large coordination numbers (6.6) and bond distance (2.94 Å) associated with this shell suggest the formation of an oxidic phase different from the CuO or Cu₂O phases.

BM_{CO2} presents a totally different structure than the other materials with 1.8 Cu at 2.55 Å that corresponds to the typical Cu-Cu distance of Cu metal (2.56 Å).

At Zn K-edge, FT profiles of BM_{CO2} and BM_{SA+CO2} match that of bulk ZnO whilst that of BM_{SA} differs significantly from the other two at high R . This picture is confirmed by the EXAFS refinements that show that Zn-O and Zn-Zn bond distances in these two materials correspond to those in bulk ZnO. In both materials ball-milled with CO₂, the fit was greatly improved by adding a carbon shell of 1.2 - 1.4 atoms at 3.06 Å, indicating the formation of carbonates. In BM_{SA} the oxygen coordination number has increased to 4.4 whereas the Zn-O bond distance of 1.98 Å is significantly longer than that found in BM_{SA+CO2} and BM_{CO2}. This may suggest the presence of a mixture of ZnO with four-fold coordination and another phase in which Zn has a six-fold coordination. This assumption is confirmed by the presence of a second shell of 2.4 Zn/Cu atoms at 2.97 Å, which does not correspond to the first Zn-Zn bond distances (3.19 and 3.24 Å) in

bulk ZnO either. A plausible interpretation of these elements combined with the XRD data [3] is the formation of a highly disordered Cu_{1-x}Zn_xO-type solid solution based on the incorporation of a large amount of Zn²⁺ in the Cu oxide matrix while the Cu-oxidation state changes from Cu¹⁺ to Cu²⁺. In this rock salt-like structure that has never been reported before, Zn and Cu feature both an octahedral coordination but with different geometries [3].

In summary, combination of HRTEM, XRD and XAFS results shows that in BM_{CO2}, ball milling induces the disproportionation of part of Cu₂O into metallic particles. These particles are protected from oxidation by a rather amorphous Cu₂O-type oxide interface layer and a CuO-type shell. These aggregates coexist with a nanocrystalline ZnO-type phase that may form a mixed amorphous carbonate interface at the surface of the CuO phase. In BM_{SA+CO2} a similar morphology is formed, except that the presence of SA induces the oxidation of a large part of the Cu¹⁺ into Cu²⁺ with no Cu metal formed. In BM_{SA} the Cu phase is almost completely oxidized to Cu²⁺ and consists of a distorted rock salt-like Cu_{1-x}Zn_xO solid solution, some amorphous CuO-type phase and the remaining nanocrystalline ZnO phase.

CONCLUSION

The use of XAFS to investigate new highly mixed phases in mechanically milled Cu₂O/ZnO materials has proved to be a crucially complement to the diffraction techniques applied earlier. Formation of a highly mixed Cu/Zn oxidic disordered solid solution was shown for the first time and indicates that the Cu/Zn interaction in the Cu/ZnO system may be much stronger than generally assumed.

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