

XPS Study on the Low-Temperature CO Shift Reaction Catalyst

I. The Unreduced Copper-Zinc System

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X-Ray photoelectron spectroscopy has been used to study Cu-Zn catalysts for the low-temperature CO shift reaction before activation by reduction. Samples with Cu concentrations in the range 3-54% of the total cations and calcination temperatures up to 923 K have been investigated. Single-phase and multiphase precipitates have been compared, showing that several chemico-physical properties are different in the two cases. Evidence has been reached for the existence, in a narrow range of temperatures, of a nonequilibrium solid solution of Cu(II) in ZnO. Also the formation of a solid solution of Zn(II) in CuO has been suggested. © 1984 Academic Press, Inc.

INTRODUCTION

Catalysts used in the low-temperature CO shift (LTS) reaction or low-pressure methanol synthesis in industrial plants are both based on formulations containing CuO, ZnO, and Al₂O₃ (or Cr₂O₃) (1-3). Before reaction, catalysts are activated by reduction of the copper species. The oxide composition used in the two processes are quite different, coming from Cu:Zn:Al = 30:50:20 (atomic) for LTS reaction to 50:30:20 (atomic) for CH₃OH synthesis.

It has been suggested that the active phase consists of highly dispersed Cu metal supported on ZnO and alumina (4), but other authors (5) have observed, in reaction conditions, a decrease in the amount of the metallic copper, which transforms to an oxidized form possibly consisting of Cu(I) not revealed by X-ray diffraction. In an extensive investigation on the methanol synthesis Cu-Zn-Al catalysis, Herman *et al.* (6) have provided good evidence for the formation of a solid solution of Cu(I) in ZnO. This solid solution was considered to be the active phase for the methanol synthesis reaction.

We have prepared very active LTS catalysts, with and without Al₂O₃, using a single-phase Cu-Zn precursor, and have concluded that in our case the active phase is a separate cuprous phase (7). In the recent literature (7-9), interactions among phases constituting the binary or ternary systems have already been observed or suggested, either before or after activation by reduction. To clarify the nature of such interactions, we have carried out an extensive investigation, mainly by X-ray photoelectron spectroscopy (XPS).

In the present paper, we are concerned with the binary Cu-Zn system before activation. In the subsequent paper (10), we shall refer to the effects of the addition of alumina and of reduction and catalytic reaction.

EXPERIMENTAL

Samples were prepared by precipitation, adding an aqueous solution of Na₂CO₃ and NaOH to an aqueous solution of copper and zinc nitrates. Suitable amounts of nitrates were used in order to obtain final concentrations of copper in the range 0-50% expressed as Cu/(Cu + Zn) atomic percentages. Precipitates were filtered,

TABLE 1
Composition Data of Cu-Zn Catalysts

Sample	Bulk composition			Surface composition			
	Zn(wt %)	Cu(wt %)	Cu/Zn (atomic %)	O	Zn (atomic %)	Cu	Cu/Zn
C3	57.1	1.7	0.034	70.8	28.0	1.2	0.043
C5	56.1	2.9	0.058	65.3	32.9	1.8	0.055
C10	52.7	6.0	0.111	61.5	35.4	3.1	0.088
C16	49.7	9.0	0.184	52.1	42.6	5.3	0.124
C31	40.2	18.0	0.459	60.0	28.5	11.5	0.404
C54	26.7	30.5	0.854	57.0	26.1	16.9	0.648
PC25	58.7	19.1	0.335	56.1	38.0	5.9	0.155

washed with hot distilled water until the disappearance of Na(I) ions, and dried at 383 K overnight. Small fractions from the same batch were calcined for 6 h at increasing temperatures (up to 923 K).

With the aim to study the influence of the phase composition of the precursor precipitate on the chemico-physical characteristics of the final catalyst, a sample was prepared using a slightly different method, where Na_2CO_3 was the only precipitating agent. In this way, more than one phase is obtained in the precipitate.

The XP spectra have been measured on a Physical Electronics PHI Model 548 spectrometer, using Mg $K\alpha$ radiation at a pressure near 2×10^{-7} Pa. Specimens have been prepared by pressing powdered samples on pure In foil (11). The spectrometer was connected to a PDP 11/50 computer (Digital Equipment Co.) for performing the collection of experimental data by signal averaging and some preliminary processing such as smoothing, background subtraction, and intensity integrations (12). Further data processing such as curve fitting and visualization was made using the GMS (Graphic Mathematical System) program (13) after transfer of digital data to a UNIVAC 1100/20 computer.

An electron flood gun has been used to compensate electrostatic charging of samples, and the C 1s binding energy value of 285.0 eV has been used as a reference level.

RESULTS

Chemical analyses of samples after drying are reported in Table 1. Using the same notation as in Ref. (7), they are identified by symbols C3, C5, . . . C54, containing respectively 3, 5, . . . 54% atoms of copper with respect to total cations. Another sample is called PC25 (polyphasic 25% at. Cu).

X-Ray diffraction (XRD) of samples C3 to C31 showed the presence of only one phase. The XRD diagram of this phase is the same as the one of hydrozincite $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ (ASTM 19-1458) obtained for the precipitate without copper. Thus we assumed for these samples the formula $(\text{Zn}, \text{Cu})_5(\text{CO}_3)_2(\text{OH})_6$, in spite of the fact that with the same formula the mineral aurichalcite is registered (ASTM 17-743). The diagram of the latter compound, however, which is a mineral and not a synthesis product, shows in the low-intensity peaks small differences not present in our diagram. Sample C54 showed the presence of a further phase, copper hydroxide nitrate $\text{Cu}_2(\text{OH})_3\text{NO}_3$ (ASTM 15-14). Sample PC25 contains, besides hydrozincite, the hydroxycarbonate $\text{Zn}_4\text{CO}_3(\text{OH})_6 \cdot \text{H}_2\text{O}$ (ASTM 11-287) and small quantities of ZnO and CuO.

After calcination at 588 K, all samples prepared by the standard method showed complete bulk decomposition of the hydrozincite phase, since only CuO and ZnO dif-

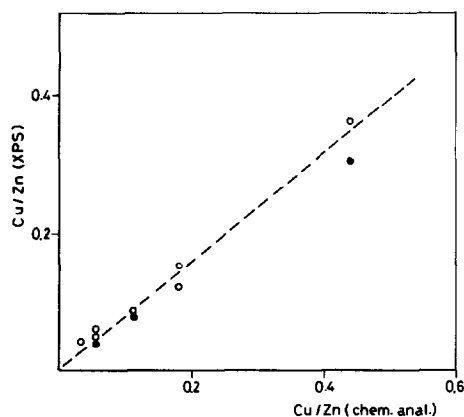


FIG. 1. Surface vs bulk Cu/Zn atomic ratios obtained from $2p$ (open circles) or $3p$ (black circles) photoemission peaks.

fraction lines were observed. Calcined samples coming from a single-phase precursor had total specific surface areas (SSA) near $50 \text{ m}^2\text{g}^{-1}$ and crystallite sizes of 15–20 nm for ZnO and 6–8 nm for CuO, calculated using the Scherrer formula (14). In sample C54, the sizes were, respectively, 90 and 40 nm and the SSA $10 \text{ m}^2\text{g}^{-1}$. This proves that there is an influence of the precursor nature on the oxide morphology. Sample PC25 was found to be more stable against calcination, since hydroxycarbonate lines were still present in the XRD pattern at 588 K.

Surface compositions of the C-series, calcined at 588 K and calculated from the O $1s$, Cu $2p_{3/2}$, and Zn $2p_{3/2}$ photoemission peak intensities using the elemental sensitivity factors method (15), gave rise to a linear relationship with the bulk compositions. In Table 1 surface compositions are reported and in Fig. 1 the relationship between surface and bulk Cu/Zn ratios for samples heated at 573 K is shown. In the same figure, some Cu/Zn ratios calculated from the Cu $3p$ and Zn $3p$ peaks are also reported. In this case, sensitivity factors derived from the empirical relationship between f_x/σ_x and E_x have been used, where f_x is the tabulated factor (15) for the photoemission transition x , σ_x the photoelectron cross section (16) and E_x the corresponding

binding energy. Values of 0.40 for Cu $3p$ and 0.46 for Zn $3p$ have been used, obtaining Cu/Zn atomic ratios quite similar to those derived from the $2p$ lines. Furthermore, experimental values agree within 20% with those expected, suggesting that the surface and bulk of such samples have similar compositions. The small systematic deviation can be ascribed to a matrix effect on the sensitivity factors, which were derived from measurements on metals.

Surface atomic ratios of some samples have been followed as a function of the calcination temperature. Results are reported in Fig. 2. The cation concentration ratios are seen to be approximately constant up to about 723 K. On samples calcined at a higher temperature, Cu/Zn decreases. The polyphasic PC25 sample constitutes an exception mainly for two reasons: (1) experimental Cu/Zn values are always lower than expected, and (2) their dependence on temperature is quite weak.

No chemical shifts of the Cu $2p_{3/2}$ photoemission peaks have been observed during calcination. The binding energy assumed the value of $933.4 \pm 0.2 \text{ eV}$, typical of CuO (15). These peaks are normally accompanied by strong satellites at $+7.9 \pm 0.1$ and $+10.4 \pm 0.1 \text{ eV}$ with respect to the main peak (Fig. 3), previously assigned to a ligand-to-metal transition: O $2p \rightarrow$ Cu $3d$ (17, 18). The existence of two shake-up sat-

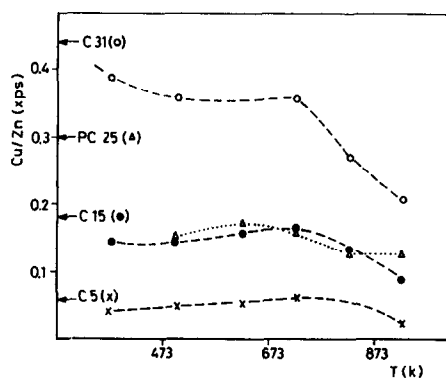


FIG. 2. Variation of the Cu/Zn surface ratios with the calcination temperature. Arrows indicate the expected values on the basis of chemical analysis.

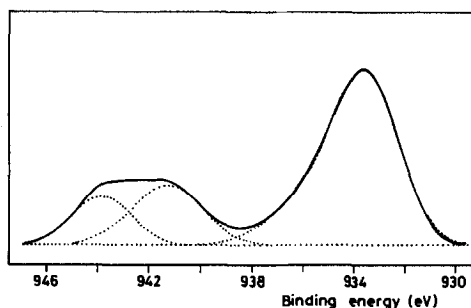


FIG. 3. Cu $2p_{3/2}$ photoemission peak of pure CuO.

ellites has been attributed to the Jahn-Teller effect (17). It is also suggested that their number depends not only on the symmetry of the environment of Cu(II) ions but also on the coordinating atoms (19).

We observed variations of the relative intensity of the satellites with respect to the main peak, depending on the Cu content. In Fig. 4 we report the satellite/main peak intensity ratio (s/m), as a function of composition, for the C-series samples calcined at 500 K. In the same figure, the results of similar measurements made on the CuO-MgO system by us and by Oku and Hirokawa (19) are reported. A decrease of the s/m ratio with respect to the value typical of pure CuO is apparent in samples having a Cu content in atoms $\leq 30\%$. The "normal"

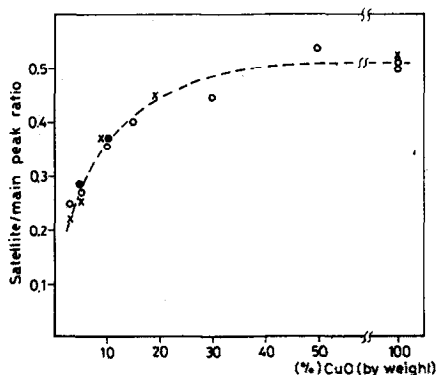


FIG. 4. Dependence of the satellite-to-main peak ratio of Cu $2p_{3/2}$ on the Cu amount contained in the samples. \circ , Cu-Zn system; \bullet , Cu-Mg system; \times , Cu-Mg system (19).

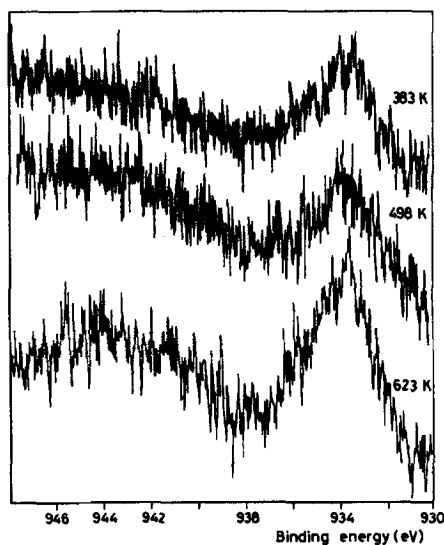


FIG. 5. Rough Cu $2p_{3/2}$ peaks of the C5 sample heated at different temperatures.

intensity ratio is rapidly restored by heating the samples at a higher temperature. After calcination at 623 K, values near 0.50 have been found for all compositions. In Fig. 5, the experimental profiles of the Cu $2p_{3/2}$ peak of sample C5 are reported after calcination at increasing temperatures. For sample PC25, s/m ratios assumed values near that of pure CuO in the whole temperature range examined ($s/m = 0.48$ at 500 K).

During calcination, we observed broadening of the Zn $2p$ peak profiles on their low energy side. Such broadening appeared at a temperature as low as 623 K and showed a tendency to disappear near 823 K. The phenomenon can be described by reporting the full widths at half maximum (FWHM) of peaks as a function of temperature (Fig. 6b). For the sake of comparison, FWHMs measured on pure zinc hydroxycarbonate during its thermal transformation to oxide are also reported (Fig. 6a). Broadening has been observed for all binary samples, PC25 included, but no correlation was observed between its extent or temperature of appearance and composition.

The analysis of the profiles showed that they can be fitted by two Gaussian compo-

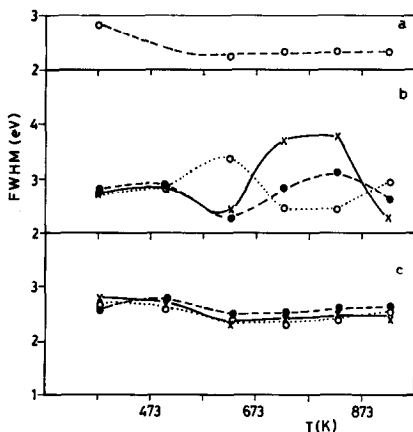


Fig. 6. Dependence of the Zn $2p_{3/2}$ FWHM values on the calcination temperature. (a) pure ZnO; (b) Cu-Zn samples (\times , C5; \bullet , C16; \circ , C31); (c) Gaussian component at 1022.2 eV on samples as b.

nents of comparable FWHM (Fig. 7), one centered at the binding energy of ZnO (1022.2 ± 0.2 eV) (15), the second having a shift of 1.7 ± 0.2 eV toward lower values. The intensity of the latter can greatly exceed that of the former. Both components assumed FWHM values near 2.6 ± 0.2 eV, comparable to that of pure ZnO. Those related to the component at the ZnO binding energy are reported in Fig. 6c.

All measurements were made with the electron gun switched on, 1 mA emission and no bias. By applying an increasing bias, we were able to obtain in all cases a single photoemission peak, having a symmetrical profile and a FWHM near 2.6 eV.

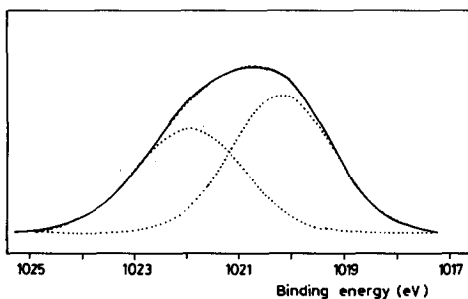


Fig. 7. Zn $2p_{3/2}$ photoemission peak of sample C31 heated at 623 K.

DISCUSSION

Single-Phase Samples

As previously reported (7), we have been able to control the precipitation method so as to obtain a single-phase precursor, having the hydrozincite structure. Only the sample with the maximum Cu loading, C54, was found to be biphasic by XRD. In fact, it contains also some copper hydroxynitrate $\text{Cu}_2(\text{OH})_3\text{NO}_3$. For the other samples, which incidentally are those of interest for the LTS reaction, we can consider that Cu and Zn are very intimately mixed. The correspondence observed between bulk and surface composition further supports this conclusion.

By heating at temperatures which are relatively low (near 500 K), hydroxysalts decompose readily to oxides, increasing the particle dispersion by a factor of five (7).

For the system CuO-MgO, where the dissolution limit of the first oxide in the second is around 15% (20), Oku and Hirokawa (19) considered the lowering of the s/m ratio with respect to pure CuO as an indication of the existence of a solid solution of CuO in MgO. It is very likely that the low s/m values observed in the CuO-ZnO system (Fig. 4) have the same cause, that is the dissolution of some cupric oxide in zinc oxide. For the latter system, a very low solubility (below 3% at. Cu) was previously found in samples fired at 1273 K for 140 h (21). In a more recent work, however, a dissolution of 2-4% CuO in ZnO in samples similar to ours and calcined at 623 K has been proposed on the basis of quantitative XRD measurements (6). We obtained similar XRD results for our samples. Furthermore, radial distribution measurements on the same system after calcination at 623 K have been interpreted in the same way by Ketchik *et al.* (9). These authors attribute the formation of the solid solution to structural distortions in the oxide lattice due to the incomplete removal of OH^- and CO_3^{2-} groups. Actually we observed on the surface of our samples some components of

the C 1s and O 1s peaks which can be attributed to carbonate and hydroxide, respectively. However, in our opinion, also and indeed mainly the structural disorder arising from the precursor decomposition at a relatively low temperature can justify the formation of a metastable oversaturated solution of divalent copper in ZnO, by analogy with other coprecipitated systems such as $\text{RuO}_2\text{-Al}_2\text{O}_3$ (22). The presence of structural disorder is supported by the broadening observed in the X-ray diffraction lines, while the increase of the s/m ratio with the heating temperature is in agreement with the nonequilibrium character of the solid solution.

By heating above 600 K, broadening of the Zn 2p peaks has been observed, which can always be decomposed into two Gaussian components (Fig. 7). Calcination at higher temperatures (≥ 823 K) gives rise to a significant lowering or disappearance of the phenomenon. A change in the oxidation number of zinc is very unlikely: Zn(I) species are unknown and the improbable formation of Zn(0) by heating in air at a relatively low temperature should not give rise to the observed shift of -1.7 eV. On the other hand, the fairly narrow temperature range of occurrence of the new component, the constancy of its position in the electron energy scale, its absence in samples not containing Cu and the possibility to obtain a single-component peak varying the bias of the electron flood gun suggest, first, that the phenomenon is not an accidental artifact and, second, that it could represent a final effect caused by some Zn(II) in a special electrical condition. Since pure ZnO treated in the same way does not show such a behavior, it must be connected with the presence of Cu.

As some Cu remains in ZnO in the first stages of the hydroxycarbonate decomposition, we can envisage that some Zn remains in CuO as a supersaturated solid solution. Such a possibility has already been suggested (9), although without strong experimental evidence. By heating for a sufficient

time at a high enough temperature, small islands of ZnO can form, surrounded by CuO. Such ZnO clusters can be electron-deficient with respect to the surrounding CuO particles. As a consequence, their surface could charge positively, the work function for the extraction of the photoelectron would decrease and thus the kinetic energy of the Zn 2p electrons would increase. IRS experiments on the same samples showed that ZnO loses its semiconductor properties due to the presence of Cu (23). Further heating causes the growing of the ZnO particles which segregate to the surface, in agreement with the observed decrease of the Cu/Zn ratios (Fig. 2). In this process, the zinc species come out from the above-described special situation. In fact, the Zn 2p_{3/2} peak becomes again symmetric and single.

The 50 K increase of the temperature at which the CuO reduction starts in copper-zinc catalysts with respect to pure CuO (9), and the slower reduction rate of binary samples, in spite of their lower average particle size compared with copper oxide (24), can also be explained by the formation of a metastable solid solution of Zn(II) in CuO.

Polyphasic Sample

The surface composition of sample PC25 shows at all calcination temperatures a preferential location of Zn at the surface. This observation suggests that the second main phase, $\text{Zn}_4\text{CO}_3(\text{OH})_6 \cdot \text{H}_2\text{O}$, covers the copper-zinc hydrozincite phase.

The Zn enrichment found in the C-series samples after high-temperature calcination and attributed to the segregation of ZnO previously in solid solution with CuO, cannot be observed for the same reason.

The presence of more than one phase seems also to have an influence on the s/m intensity ratios, that is on the amount of solid solution of Cu(II) in ZnO, thus confirming that the occurrence of phases plays an important role in several chemico-physical characteristics of such catalysts. Also the presence of some free CuO in the pre-

cipitate can contribute to the high s/m values.

Note added in proof. After sending this work, two papers have been published on a very similar argument, concerning an extensive surface characterization by XPS of CuO–ZnO methanol synthesis catalysts [Okamoto, Y., Fukino, K., Imanaka, T., and Teranishi, S., *J. Phys. Chem.* **87**, 3740; 3747 (1983)]. Strong oxide–oxide interactions were observed in the coprecipitated catalysts, as in our case, and the dependence by composition of the Cu satellite-main peak intensity ratio was fully confirmed. Also the surface composition results appear comparable. The lack of observation of variations of the Zn $2p_{3/2}$ peak should be due to the fact that precursor samples are not single-phase but polyphasic.

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