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XPS Study on the Low-Temperature CO Shift Reaction Catalyst

II. The Effects of the Addition of Alumina and Reaction Conditions

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The work described in Part I (Garbassi, F. and Petrini, G., *J. Catal.* 90, 106 (1984)) on binary Cu–Zn catalysts for the low-temperature shift of CO before activation and reduction has been supplemented in the present study by X-ray photoelectron spectroscopy of the effect of the addition of alumina and of reaction conditions. It has been found that the surface composition strongly depends on the preparation method. Also, during the shift reaction itself the copper concentration of most of the catalysts increases and the chemical state changes, as evidenced by a decrease of the satellite-main peak ratio. XPS has proved to be a good diagnostic method for commercial ternary samples.

INTRODUCTION

In Part I (*1*) we have characterized, mainly by XPS, several binary catalysts for the low-temperature CO shift (LTS) reaction.

Strong evidence was reached for the formation, during the calcination steps at increasing temperatures, of a solid solution of Cu(II) in ZnO. Also the formation of a solid solution of Zn(II) in CuO has been suggested, on the basis of the analysis of the Zn photoemission peaks. Such results confirm and complete recent literature on Cu–Zn catalysts (*2–4*). Furthermore, we have shown that it is important for the chemicophysical properties (*1*) and the catalytic behavior (*2*) of the samples to start from a single-phase precursor.

In this part of the work, we have investigated, mainly by XPS, the role of alumina on the properties of catalysts. Some commercial ternary catalysts have also been examined. Finally, the effect of the LTS reaction on the surfaces of samples, both laboratory-prepared or commercial, have been investigated.

EXPERIMENTAL

A ternary Cu–Zn–Al sample has been prepared by precipitation, by first obtaining a single-phase hydrozincite powder, then adding a suitable amount of $Al(OH)_3$ (*2*). The sample is named CA26 (26% at. Cu plus alumina). A second catalyst, PCA24 (polyphasic 24% at. Cu plus alumina), has been prepared in a standard way but starting from a polyphasic precipitate, having the phase composition of PC25 (*1*). Finally, a third sample has been prepared by coprecipitating all three cations by a method similar to that used for binary catalysts (*1*). This sample is called TCA23 (ternary 23% at. Cu plus alumina).

Three commercial ternary catalysts have also been examined (1COM, 2COM, and 3COM), corresponding to samples 1–3, respectively, in the paper of Vlaic *et al.* (*5*). 1COM, available also as a dried powder, has been calcined for 6 h at three different temperatures between 673 and 873 K.

XPS spectra have been collected and processed by means of instruments and methods already described (*1*).

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TABLE 1

Bulk Composition of Cu–Zn–Al Catalysts

Sample	Cu	Zn	Al	Cu/Zn	Al/Zn
	(atomic %)				
CA26	26	56	18	0.45	0.32
PCA24	24	58	17	0.42	0.29
TCA23	23	56	21	0.41	0.38
1COM	26	49	25	0.52	0.51
2COM	32	48	20	0.66	0.42
3COM	28	53	19	0.53	0.17

TABLE 2

X-Ray Pattern of Sample TCA23

d (Å)	Relative intensity
12.26	10
9.33	15
7.50	35
7.15	100
4.92	12
4.44	55
3.808	20
3.496	10
3.345	30
2.806	12
2.630	50
2.455	30

The catalytic reaction has been carried out in a standard flow reactor, after reduction with 0.5–3.0% H_2 in N_2 flow up to 503 K. Activity runs have been performed at a pressure of 1×10^5 Pa and in the temperature range 453–503 K. The gas mixture composition was 3%, CO, 15% CO_2, 58% H_2, and 24% N_2. The molar ratio between H_2O and the gas mixture was maintained equal to 0.5.

RESULTS

Chemical analyses of samples investigated in this work are reported in Table 1. X-ray diffraction showed that calcination at 500 K was sufficient to give rise to the complete decomposition of sample CA26 to ZnO and CuO, while the compound (or compounds) containing aluminum remained amorphous. Sample PCA24, on the contrary, behaved like PC25, showing only partial decomposition. The coprecipitation ternary catalyst, TCA23, showed an X-ray diffraction pattern probably attributable to a single phase, but not corresponding to any known compound. The list of measured *d* values is reported in Table 2 and studies aimed at a better structural characterization are in progress.

Surface compositions derived from XPS intensities are reported in Table 3. The Cu/

TABLE 3

Surface Composition of Cu–Zn–Al Catalysts

Sample	T^a (K)	O	Cu	Zn	Al	Cu/Zn	Al/Zn
		(atomic %)					
CA26	623	52.2	11.9	35.9	n.d.	0.33	—
PCA24	623	53.9	9.8	36.3	n.d.	0.27	—
TCA23	593	62.6	5.0	23.1	9.3	0.22	0.40
1COM	673	62.5	9.0	19.0	9.5	0.47	0.50
	773	62.3	7.9	17.9	11.9	0.44	0.66
	873	64.5	6.3	19.4	9.8	0.32	0.51
2COM	—	62.6	11.1	18.5	7.8	0.60	0.42
3COM	—	54.1	10.7	35.0	0.2	0.31	0.01

[a] Calcination temperature.

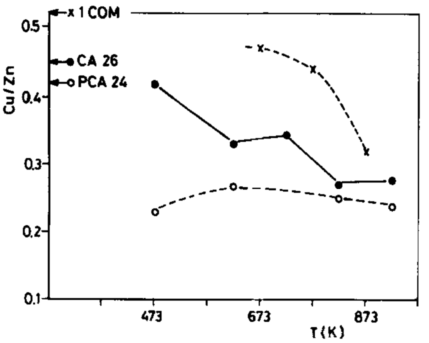

FIG. 1. Variation of the Cu/Zn surface ratio with calcination temperature. Arrows indicate the expected values on the basis of chemical analysis.

TABLE 4

Satellite-to-Main Peak Intensity Ratios (s/m) of the Cu $2p_{3/2}$ Transition and Full Widths at Half Maximum (FWHM) of the Zn $2p_{3/2}$ Transition

Sample	T^a (K)	s/m	FWHM (eV)
CA26	623	0.50	3.0
PCA24	623	0.36	3.4
TCA23	593	0.32	2.5
1COM	673	0.35	2.4
	773	0.20	2.4
	873	0.13	2.6
2COM	—	0.24	2.4
3COM	—	0.24	2.2
C31^b	623	0.43	3.4

^{a} Calcination temperature.
^{b} From Ref. (*1*).

Zn ratios as function of the calcination temperature are shown for some of the samples in Fig. 1. Sample PCA24 shows an experimental Cu/Zn ratio considerably lower than that expected on the basis of chemical analysis and approximately dependent of the calcination temperature. The Cu/Zn value of sample CA26 decreases monotonically as a function of calcination temperature from a ratio approximately equal to that determined by chemical analysis. This overall behavior parallels that shown by the corresponding binary catalysts, that is PC25 and C31, respectively (*1*).

The sample TCA23, prepared by ternary coprecipitation, has a behavior similar to that of coprecipitated binary compounds.

Satellite-to-main peak ratios (s/m) of the Cu $2p_{3/2}$ peaks and full widths at half maximum (FWHM) of the Zn $2p_{3/2}$ peaks are reported in Table 4. Results obtained on a binary compound of similar Cu content (C31) are also reported for comparison. Samples can be divided into two groups, one comprising TCA23, 1COM, and 2COM, having low s/m ratios and low FWHMs, and another comprising CA26 and PCA24, with high values of s/m and FWHM (similar to C31).

Several samples have been analyzed by XPS also after low-temperature CO shift reaction runs in the laboratory. Before discharging a catalyst sample, its surface was passivated by means of a 0.5% O_2 in N_2 flow at room temperature. This treatment prevented a fast uncontrolled reoxidation of the samples.

Volume rate constants k_V and specific rate constants (per gram of Cu) k_s are reported in Table 5.

Surface compositions and other XPS features measured after reaction are reported in Table 6. By comparison with Tables 3 and 4 it is quite apparent that after reaction the Cu/Zn ratio increases significantly (sample 2COM, which had a high Cu/Zn ratio before reaction, is an exception), while the s/m ratio decreases. The FWHMs of the Zn $2p_{3/2}$ peaks, except 2COM, are

TABLE 5

Activity Data of Cu–Zn–Al Catalysts

Sample	T^a (K)	k_V (s^{-1})	k_s ($s^{-1}g^{-1}$)
PCA24	623	2.75	4.28
TCA23	593	1.20	1.80
1COM	673	1.38	2.85
2COM	—	1.82	2.80
3COM	—	2.88	3.82

^{a} Calcination temperature.

TABLE 6

XPS Results on Ternary Catalysts after LTS Reaction

Sample	T^a (K)	O	Zn	Cu	Al	Cu/Zn	Al/Zn	s/m Cu $2p_{3/2}$	FWHM (eV) Zn $2p_{3/2}$
		(atomic %)							
TCA23	593	65.5	19.9	8.4	6.2	0.42	0.31	0.21	2.5
1COM	673	62.2	17.3	9.5	11.0	0.55	0.63	0.19	2.3
	773	60.0	18.9	9.8	11.3	0.52	0.60	0.24	2.7
	873	63.3	19.2	8.6	8.9	0.45	0.46	0.10	2.6
2COM	—	62.7	17.9	10.6	8.8	0.59	0.49	0.17	3.9
3COM	—	57.5	28.7	13.6	0.2	0.47	0.01	0.13	2.2

[a] Calcination temperature.

small before and after reaction, indicating one chemical state of Zn. The Zn $2p_{3/2}$ peak of 2COM is considerably broader after reaction.

DISCUSSION

Taking into account the results reported in Tables 3 and 4, particularly those pertaining to laboratory samples, the preparation methods of which are known in detail, we can note that CA26 and PCA24, both prepared by coprecipitation of Cu and Zn salts and subsequent addition of $Al(OH)_3$ gel, show quite similar characteristics. In both samples Al is absent on the surface and the s/m and FWHM values are high. On the other hand, there is some difference in the behavior of Cu/Zn with heating (Fig. 1). In fact PCA24 shows values which are always low, while CA26 exhibits a gradual decrease.

We recall that the two samples differ in respect of the crystalline phases of the precipitation product. CA26 contains hydrozincite only, while PCA24 contains hydrozincite and zinc hydroxycarbonate, just as do the corresponding binary samples (*1*). The low Cu/Zn ratio for the polyphasic sample suggests, as in Part I (*1*), that the phase containing both Zn and Cu is covered by the phase containing Zn only.

For the samples 1COM and 2COM, we have obtained results opposite to the foregoing: there is a good correspondence between the surface and bulk atomic ratios and low values of s/m and FWHM. TCA23 behaves similarly, but has a quite low Cu/Zn ratio, while the properties of 3COM are intermediate between this group (1COM, 2COM, and TCA23) and the group consisting of CA26 and PCA24. In fact, 3COM shows low s/m and FWHM values, while the surface composition is very different, with Al nearly absent and Cu/Zn low.

Recalling the results as a whole and the interpretations given in Part I (*1*), namely that a low s/m indicates a solid solution of Cu(II) in ZnO and a high FWHM is considered to be the consequence of the destruction of a previous solid solution of Zn(II) in CuO, the following considerations can be made:

(1) By addition to the catalyst of the aluminum compound after coprecipitation we obtain a product whose surface does not contain this cation. Even though alumina is generally considered to be a structural promoter and not to participate in the active phase (*6*), this fact could be relevant for the subsequent catalytic behavior. Our results suggest also that the sample 3COM could have been prepared in a similar way. On the other hand, ternary coprecipitation gives rise to high Al/Zn ratios, as in samples TCA23 and 1COM. By analogy, sample 2COM could have been prepared by ternary coprecipitation, too.

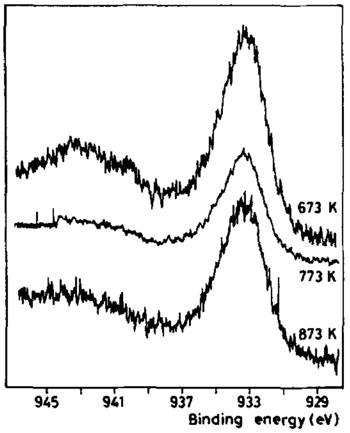

FIG. 2. Rough Cu $2p_{3/2}$ peaks of the sample 1COM after calcination at different temperatures.

(2) The presence of aluminum in the catalyst favors the formation of a solid solution of Cu(II) in another phase, since s/m values are always lower than those of binary samples with similar Cu/Zn ratios. This is true particularly for samples prepared by ternary coprecipitation, and also for 3COM. Theoretically, the solvent for divalent copper should be ZnO or alumina. A promoting action of alumina for a further dissolution of Cu(II) in ZnO seems likely only if Al(III) ions participate in the mixed phase. In our opinion, this is improbable, even though we cannot exclude it completely. On the other hand, the possibility of interactions between cupric ions and alumina has already been studied by several chemico-physical techniques (see Ref. (*7*) and references therein). In some conditions, a binding energy of Cu near 934.6 eV has been observed and attributed to the spinel $CuAl_2O_4$. However, such a spinel is not stable with respect to the parent oxides at temperatures lower than 895 K (*8*), and was not found in some of the present samples by XANES and EXAFS (*5*). We have not observed significant chemical shifts of the Cu $2p$ peaks. On the other hand, measuring the FWHMs of the same peaks, we have found in two samples, 1COM heated at 873 K and TCA23, values of 3.3 and 4.0 eV, respectively, larger than the average value of 2.9 ± 0.2 eV. This observation, as well as the fact (Fig. 2) that s/m decreases with calcination temperature (thus ruling out that nonequilibrium CuO–ZnO solid solution is responsible) and the parallel decrease of Cu/Zn and Al/Zn on the sample heated at 873 K with respect to that heated at 773 K, suggest that at least a superficial formation of islands of a Cu–Al compound is likely.

(3) The samples having a marked Al surface concentration did not show broadening of the Zn $2p$ peaks. Two interpretations are possible, either that the solid solution of Zn(II) in CuO is more stable to temperature or that it does not occur at all. At the present stage of the research we cannot give a definitive interpretation.

The combined effects of activation by reduction and reaction on the surface of catalysts do not seem to cause important modifications. Sample 2COM shows a broadening of the zinc FWHM and all the Cu/Zn ratios show a tendency to increase. Other XPS features, such as Al/Zn ratios and FWHMs, remain constant, suggesting a remarkable stability of the system in reduction or reaction conditions. The generalized lowering of the s/m values is probably due to the presence of some residual Cu(I) in the discharged catalyst. Some broadening of the main peak is consistent with this interpretation. The fact that copper is the only reducible species is probably connected with the increase of its surface concentration.

Activity data (Table 5) give a clear indication that the surface characteristics, and therefore the preparation procedure, affect the catalytic behavior. In fact, on the basis of the k_s values, the following activity scale can be drawn

$$\text{PCA24} \geq \text{3COM} \gg \text{1COM} \simeq \text{2COM} \gg \text{TCA23}.$$

The two catalysts showing a negligible surface concentration of Al are much more active than the others, all prepared by ternary coprecipitation (this statement is only presumable for 2COM). Among them, TCA23 has the lowest k_s value. The latter result could depend on the very low surface Cu concentration of this sample (Table 3). The above considerations do not change substantially if one considers the k_v values instead of k_s.

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