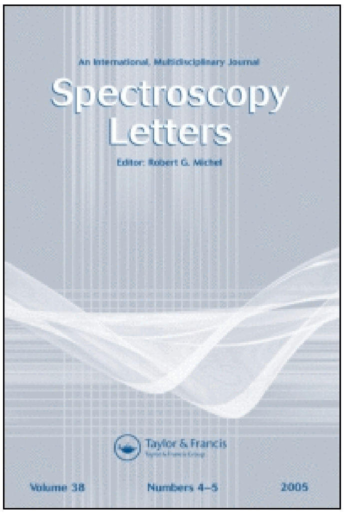

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

XPS Study of a Cu-A1-O Compound Under H_2/CO Mixture

R. Bechara[a]
[a] Laboratoire de catalyse hétérogène et homogéne URA CNRS 402 Bt. C3, Université des Sciences et Technologies de Lille, Villeneuve d'Ascq Cedex

To cite this Article Bechara, R.(1994) 'XPS Study of a Cu-A1-O Compound Under H_2/CO Mixture', Spectroscopy Letters, 27: 7, 955 — 964
To link to this Article: DOI: 10.1080/00387019408006644
URL: http://dx.doi.org/10.1080/00387019408006644

SPECTROSCOPY LETTERS, 27(7), 955-964 (1994)

XPS STUDY OF A Cu-Al-O COMPOUND UNDER H_2/CO MIXTURE

Key words : XPS, Copper, Aluminium, H_2/CO, Spinel

R. Bechara [†]

Laboratoire de catalyse hétérogène et homogène URA CNRS 402
Bât. C3, Université des Sciences et Technologies de Lille
F-59655 Villeneuve d'Ascq Cedex.

ABSTRACT

Mixed copper aluminium oxide has been studied by XPS. It was shown that the reduction under hydrogen of the precursor oxide leads to the formation of cuprous ions located in the octahedral sites of the spinel matrix γ-Al_2O_3 and hydridic species stored in the solid. The use of the pre-reduced compound at 300°C before catalysis with H_2/CO is necessary to maintain almost intact the spinel phase despite the formation of metallic copper, whereas a strong modification of a surface composition was obseved when the solid is directly treated by H_2/CO mixture.

[†] Present Address:
Laboratoire de Génie Chimique et d'Automatique (J.E. 235)
Ecole Centrale de Lille et ENSCL. Cité scientifique, B. P. 48
F-59651 Villeneuve d'Ascq Cedex.

INTRODUCTION

Mixed oxide systems associating copper with aluminium are very interesting catalytic compounds, particularly for methanol synthesis from syngas and for selective hydrogenation of dienes into monoenes (1-3). We have recently characterized Cu-Al-O solid (Cu/Al = 0.5) in order to obtain information on the surface composition as well as the reducibility with gaseous molecules such as hydrogen and carbon monoxide. Using mainly XPS (4), we have demonstrated that, in both cases, the progressive reduction of Cu^{2+} species to lower oxidation states Cu^{+} and $Cu^{\bullet}$ is observed from 250°C. Up to 300°C, the formation of metallic copper particles on a residual spinel phase was observed by X-ray diffraction. At 350°C, metallic copper supported on γ-alumina was obtained.

The copper (II) species located in tetrahedral sites are reduced to monovalent and metallic copper while the Cu^{2+} ions loacated in octahedral sites are reduced to Cu^{+} stabilized in octahedral sites. The concentration of these species depends on the reduction temperature.

In this paper, we present the results of a characterization study of a Cu-Al-O compound by XPS under H_2/CO mixture. The influence of the reduced copper species, formed during the hydrogen treatment on the stability of the spinel phase will be discussed.

EXPERIMENTAL

Solid preparation

The Cu-Al-O (Cu/Al = 0.5) solid was prepared by coprecipitation of hydroxides from a solution of copper and aluminium nitrates with progressive addition of ammonium hydroxide up to a final pH of 6.0. The Cu-Al oxide was then obtain by thermal decomposition under a flow of dried air at 900°C.

Structure

The structure of a Cu-Al-O compound was analysed using a Philips PW 1008 X-ray diffractometer equipped with a copper anode and a nickel filter.

XPS measurements

The XPS studies were performed using a Leybold-Heraeus LHS 10 spectrometer with an Al Kα anticathode (hν = 1486.6 eV). The spectrometer was equipped with three interconnected chambers. In the first preparation chamber, the sample was treated under different atmospheres. In our case, Cu-Al-O was treated with gaseous molecules such as H_2 and H_2+CO mixture at various temperatures and at atmospheric pressure. In the second chamber, the sample was degassed before being introduced into the third chamber where XPS analysis was performed. The sample was crushed into a fine powder and pressed on a stainless-steel support. The spectra were taken under a high vacuum (10^{-8} torr) at room temperature. The binding energies were determined by using the C 1s peak at 284.7 for standardization.

The surface atomic composition Cu/Al was calculated by using the following formula:

$$Cu/Al = k\ I_{Cu}/I_{Al}\ (5).$$

where I_{Cu} and I_{Al} are the areas of photoelectrons peaks (here Cu $2p_{3/2}$ with their satellite structure Cu 3s and Al 2s) of the analysed elements, k is a proportionality factor including atomic features and apparatus specifities which can be found in the literature (6).

RESULTS AND DISCUSSIONS

In a previous study, detailed XPS analysis of Cu-Al oxide compound has been reported (4). The XP spectrum of the Cu $2p_{3/2}$ level of the copper (II) ions present in the solid are generally characterized by a main peak (mp) accompanied by a satellite peak (sat). This satellite structure of Cu^{2+} compounds has been attributed to the transition of an electron from the 3d to the 4s level during the relaxation process (7) or from the ligand to metal (O 2p to Cu 3d) (8).

The Cu $2p_{3/2}$ spectrum of Cu-Al-O sample in the oxidized state (Figure 1) is typical for Cu^{2+} species in terms of both the binding energy (B.E. ~ 935.0 eV) and the presence of an intense satellite line. It has been shown that, in the case of cubic spinel, the intensity ratio I_{sat}/I_{mp} depends on the environment of the Cu^{2+} species (9); these values are 0.85 and 0.55 for the divalent copper in tetrahedral and octahedral sites respectively and should not change as long as the spinel phase is conserved.

In the case of the Cu-Al-O compound, the ratio of the intensity of the satellite peak over the intensity of the main peak is $I_{sat}/I_{mp} = 0.74$. According to the intensity ratio of I_{sat}/I_{mp} of copper (II) species in tetrahedral and octahedral sites, the calculated proportions in our compound are 67% in tetrahedral sites and 33% in octahedral sites; these values are similar to the proportion generally found in the case of copper aluminate (8). Moreover, the surface atomic composition Cu/Al deduced from the XPS lines (Cu 2p/Al 2s = 0.47 and Cu 3s/Al 2s = 0.45) shows a good homogeneity between the surface and the bulk, since both calculated values are very close to that obtained by chemical analysis (Cu/Al = 0.5). In addition all the observed XRD lines are due to the $CuAl_2O_4$ compound of a spinel structure (4).

Figure 2 and 3 show the evolution of Cu $2p_{3/2}$ spectra from the initial state (a, not treated) to the reduced state as a function of different reduction procedures.

Spectra (b), (c) and (d) correspond to the sample prereduced under hydrogen at 300°C followed by catalysis with H_2/CO mixture at various temperatures. Spectra (b′), (c′) and (d′) correspond to the solid directly treated with H_2/CO mixture.

The XP spectra of Cu $2p_{3/2}$ level of the copper (II) ions are characterized by a principal peak accompanied by a satellite peak. With increasing reduction from room temperature to 350°C, a decrease of the satellite peak is recorded; this diminuation indicates a

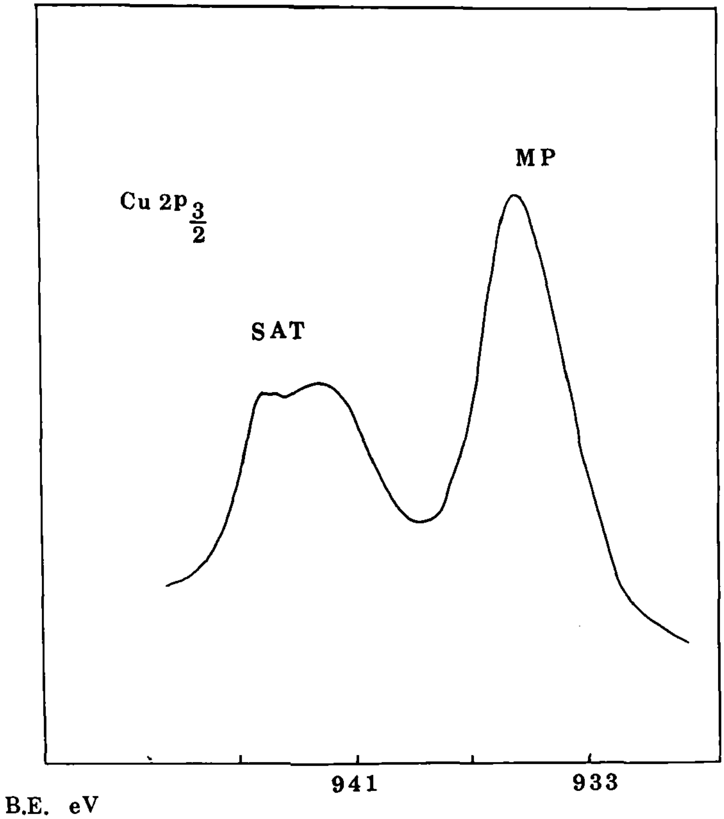

FIG. 1 :Cu $2p_{3/2}$ X-Ray Photoelectron Spectrum for Cu-Al-O (Cu/Al = 0.5) compound.

partial reduction of copper (II) species to form Cu^+ and/or Cu° species in the solid surface. Also, the binding energy decreases compared with the Cu $2p_{3/2}$ spectrum of the untreated solid where the oxidation state is + 2. Moreover, the dissymmetric shape of the principal peak might be explained by the presence of several lines attributed to bivalent, monovalent and metallic copper species.

Note that this reducing effect induced by CO/H_2 mixture appears at temperatures about 50°C higher than those required to give the same state for a pre-reduced catalyst.

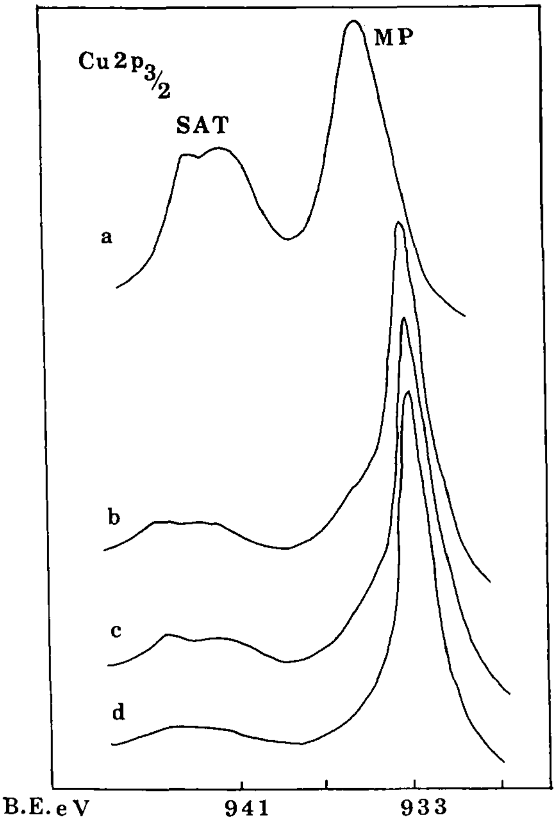

FIG. 2 :Cu $2p_{3/2}$ spectra for Cu-Al oxide : (a) in the oxidic state, (b), (c) and (d) reduced by H_2 at 300°C followed by catalysis with H_2/CO mixture at 280, 300 and 350°C respectively

More interesting is the evolution of the Cu/Al atomic ratio measured by XPS lines intensities (Figure 4). In fact, the surface composition of the precursor oxide changes when reduction is performed under hydrogen at 300°C or under the CO-H_2 mixture or by these two successive steps. In the first and the third cases, the surface atomic ratio Cu/Al does not change up to 350°C by comparison with the bulk analysis. On the contrary, when the solid is directly treated under CO-H_2 mixture, the atomic ratio sharply decreases.

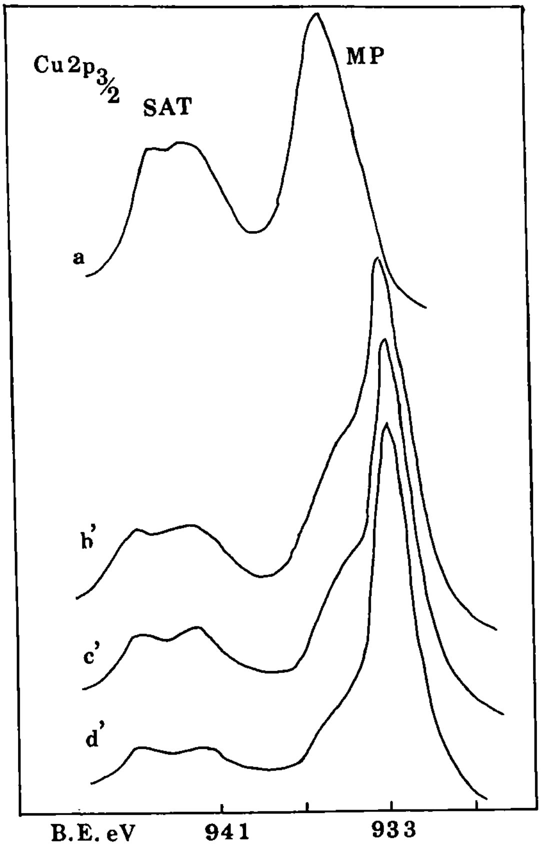

FIG. 3 :Cu $2p_{3/2}$ spectra for Cu-Al oxide : (a) in the oxidic state, (b'), (c') and (d') treated with the H_2/CO mixture at 280, 300 and 350°C directly with the oxide precursor.

Clearly, the XPS results show that the final structure of the solid depends on the eventual prereduction under hydrogen before the CO/H_2 reaction. In absence of prereduction, the surface composition is modified when the temperature increases. As the Cu/Al ratio decreases, the solid surface appears more impoverished in copper species. This can be explained by the formation of large metallic

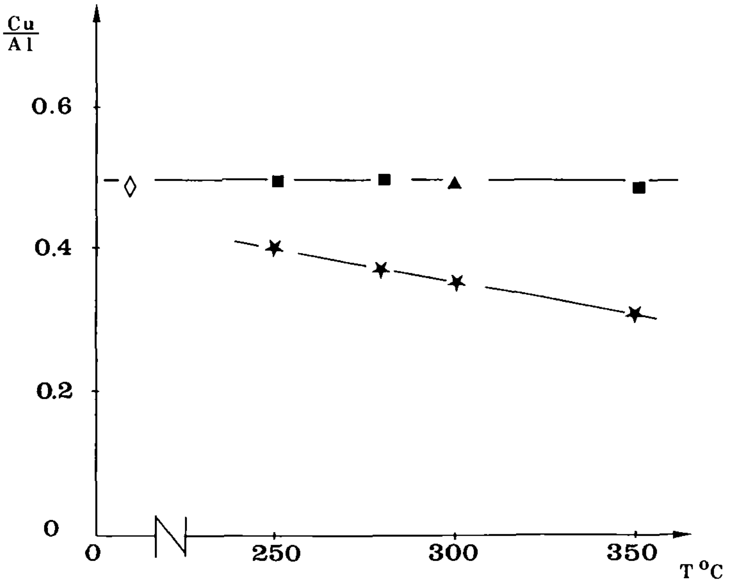

FIG. 4 :Evolution of the Cu/Al atomic ratio measured by XPS as a function of different reduction procedures:
◇ : oxide precursor
▲ : after reduction by H_2 at 300°C
■ : after reduction by H_2 at 300°C and then by H_2/CO mixture
✶ : directly treated by H_2/CO mixture.

copper critallites deposited on the surface of the spinel, which agrees with the X-ray diffraction observations (11). Hence XPS results give a clear indication of a particular spinel sructure stabilization up to 350°C for the mixed copper aluminium oxide when it has undergone reduction using H_2 before treatment with a CO/H_2 mixture.

A similar results are obtained in the case of Cu-Cr-O catalyst where a pretreatment with hydrogen before introduction of the CO/H_2 mixture is necessary to maintain the spinel phase (12). This pretreatment seems to result in the reduction of a large amount of cupric ions into cuprous ions, precisely located in the support and appears to leave the solid resistant to further reduction by the CO/H_2 mixture. This latter point is very important and agrees with the results published by other authors (13,14). These authors attribute the desactivation of a copper based catalyst to the over reduction of copper species to metallic copper. However, this class of compounds behave as hydrogen reservoirs, hydrogen being stocked in the solid as hydridic ions, whose ionic radii (1.54 Å) are similar the oxanions (OH^- : 1.76 Å and O^{2-} : 1.40 Å). Also, hydridic ions are known to play an essential role on the stability of the structure as indicated by some authors (15,16).

CONCLUSION

From the XPS results, it has been demonstrated that the surface atomic composition allows good homogeneity between the surface and the bulk to be assumed, since the calculated Cu/Al ratio are very close to that obtained by chemical analysis.

It has been shown that the step of reduction by hydrogen at 300°C before catalysis with H_2/CO is necessary to maintain almost intact the spinel phase despite the formation of small Cu° particles, whereas a strong modification of surface composition was observed when the solid is directly treated by H_2/CO mixture. These experiments may considerably help in the choice of the activation procedure of mixed oxide compounds.

REFERENCES

1. Bart J. C. J., Sneeden R. P. A., Catal. Today, 1987 ; 2 : 1.
2. Robinson W. R. A. M., Mol J. C., Appl. Catal., 1990 ; 60 : 73.
3. Jalowiecki L., Wrobel G., Daage M., Bonnelle J.P., J. Catal., 1987 ; 107 : 375.
4. Bechara R., Aboukais A., Bonnelle J. P., J. Chem. Soc. Faraday Trans., 1993 ; 89(8) : 1257.

5. Carter W. J., Schwfitzer G. K., Carlson T. A., J. Electron Spectros. Relat. Phenom., 1974 ; 5 : 827.

6. Fadley C., In Electron Spectroscopy, Theory, Techniques and Applications 2. Brundle C. R., Baker A.D. Ed., Academic press, New York 1977 : 1.

7. Robert T., Offergeld G., Phys. Status Solid., 1972 ; 14 : 277.

8. Kim K. S., J. Electron Spectros. Relat. Phenom., 1974 ; 3 : 49.

9. Bechara R., Aboukais A., Guelton M., D'huysser A., Grimblot J., Bonnelle J. P., Spectrosc. Lett., 1990 ; 23 : 1273.

10. Friedman R. M., Freeman J. J., Lytle F. W., J. Catal., 1978 ; 55 : 10.

11. Bechara R., PhD Thesis U. of Lille 1986.

12. Bechara R., Aboukais A., Hubaut R., Wrobel G., D'huysser A., Bonnelle J. P., J. Chim. Phys., 1992 ; 89 : 853.

13. Klier K., Chatikavanisj V., Herman R. G., Simmons G. W., J. Catal., 1982 ; 74 : 343.

14. Herman R. G., Klier K., Simmons G. W., Finn B. F., Bulko J. B., Kobylinski T. P., J. Catal., 1979 ; 56 : 407.

15. Nix R. G., Rayment T., Lambert R. M., Jennings J. R., Owen G., J. Catal., 1987 ; 106 : 216.

16. Owen G., Hawkes C. W., Lloyd D., Jennings J. R., Lambert R. M., Nix R. M., Appl. Catal., 1990 ; 58 : 69.

Date Received: March 17, 1994
Date Accepted: April 18, 1994