

The Role of the Coprecipitation Sequence of Salt Precursors on the Genesis of Cu-ZnO-Al₂O₃ Catalysts. Synthesis, Characterization and Activity for Low Temperature Shift Reaction

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Abstract - Cu-ZnO-Al₂O₃ catalysts for the low-temperature water-gas shift reaction were prepared using methods of direct and reverse coprecipitation. The catalysts obtained were characterized by DRX, TPR, XPS, N₂O chemisorption, Hg-Porosimetry and BET surface area. It was observed that the precipitation sequence of the precursors led to significant differences in values of copper dispersion and consequently in the activity of the catalyst for the water-gas shift reaction.

Keywords: Copper-zinc-aluminum catalysts, catalyst preparation, catalyst characterization, copper surface species, structure-activity relationship, water-gas shift reaction.

INTRODUCTION

One of the raw gas purification stages used in ammonia synthesis is carbon monoxide shift conversion with water steam at temperatures of 483 to 513 K. Due to its commercial and economic importance, the pure synthesis gas production required for the manufacture of ammonia depends largely on the water gas shift reaction. Extensive research has been carried out to develop efficient catalysts. The commercial catalyst used for the mentioned purposes consists of an intimate mixture of copper, zinc and alumina oxide (Campbell et al., 1970; Herman et al., 1979) which seems to be the most active catalyst in this field (Hawker, 1982). This catalyst is commonly prepared by coprecipitation, mixing copper, zinc and aluminum nitrate solutions with a solution of

sodium carbonate (Kalchev et al., 1995; Garbassi and Petrini, 1984) or sodium bicarbonate (Busseto and Petrini, 1984).

The most important properties of the above mentioned catalyst, such as activity, stability, etc., are likely to be dependent on dispersion of the active component, as well as on interaction with the support medium. Activity may be related to the degree of copper dispersion and linked to metal particle size. In this case, the method of preparation may have a significant effect on the dispersion and activity of the metal.

The nature of the active sites for WGS is still the subject of some controversy, with opinions divided as to the relative importance of copper surface area and Cu^{1+} cations dissolved in ZnO lattices. Hermann et al. 1979 identified the formation of a solids solution of Cu^{1+} in ZnO and suggested that these species were catalytically active. Petrini et al. 1983 used XPS to identify a solids solution of Cu^{2+} in ZnO. In these cases, it was suggested that Cu^{1+} in ZnO played some role in catalysis. On the other hand, Robinson and Mol 1990, and many other authors (Mukherjee et al., 1976; Jovanovic, 1988; Ghorai et al., 1970) have suggested that copper surface area is the critical factor. It was suggested that one of the roles of ZnO was to increase copper dispersion (Evans et al., 1983). Consequently, high copper surface area are related to small well-dispersed copper crystallites, with alumina acting mainly as a thermal stabilizing agent.

The importance of changes in structure and texture, caused by phase transformation during catalyst preparation, is closely connected to the elucidation of the specific role of components of the shift reaction. In this paper, the results of the water-gas shift reaction catalytic activity investigation and the physico-chemical properties of catalysts prepared from different precursors are presented. Phase composition of the catalyst precursors was controlled by varying the coprecipitation routes. The results of this investigation allowed us to draw some conclusions regarding the role of a precursor in the formation and structure of the active sites in the water-gas shift reaction.

EXPERIMENTAL

Catalyst Preparation

The catalysts were prepared using coprecipitation from nitrate solutions of copper, zinc and aluminum by one of the following methods:

Method one - Precursors with different atomic ratios (see [Table 1](#)) were obtained by direct precipitation. They will be referred to as **C₃Z₆A**, **C₄Z₄A₂** and **C₅Z₂A₃**. NaOH solution (0.3 M), was added dropwise to a nitrate solution (0.5 M) of each metal at 343 K, under vigorous agitation. In this way, the pH was never higher than 8.0. The solution was subsequently filtered and then washed with distilled water at about 343 K until the sodium concentration, which was determined by flame photometer, was less than 0.2 ppm. The drying temperature was 383 K. The precursors were calcined in air for 24 hours at 623 K, palletized and sieved (0.40-0.52 mm) for the characterization and catalytic runs.

Method two - In this method, three catalysts with the same composition (see [Table 1](#)) were prepared using the method of reverse coprecipitation, differing only in the precipitation steps. They will be referred to as **CZA**, **CZ-A** and **CA-Z**, respectively.

Basically, the nitrate solutions (0.4 M) of each metal were added dropwise to a Na_2CO_3 solution (0.3 M) at 353 K, in such a way that the pH was never below 8.3. Once the nitrate solutions were added, they were stirred vigorously for more than 30 minutes. The precipitate was filtered and thoroughly washed with deionized water at 353 K until the Na^+ ion concentration in the filtrate, determined with a flame photometer, was

lower than 0.2 ppm. The mixture was cooled to room temperature, and the precipitate was set aside and aged for 30 minutes. The precipitate was dried at 383 K overnight, calcined in air at 773 K for 4 h, pelletized and sieved (0.40 - 0.52 mm) for characterization and use in the catalytic reactions.

The **CZA** catalyst was prepared by the simultaneous coprecipitation of copper, zinc and aluminum. The **CZ-A** and **CA-Z** catalysts were obtained by coprecipitation of the first two metals and mixing with the third metal that had been precipitated separately. Mixing of the precipitates was always carried out prior to the washing step.

Catalytic Activity Measurements

Catalytic activity of the samples in the water-gas shift reaction was measured in a flow system at atmospheric pressure in a stainless-steel reactor. A gas mixture similar to that used in industry, which contained (vol. %) 0.25 CH₄, 16.5 CO₂, 3.2 CO, 0.23 Ar, 20.5 N₂ and 59.3 H₂ was used. The reactions were performed between 453 and 493 K, within the differential regime for conversion, and a flow rate of 4500 h⁻¹ with a steam/gas molar ratio of 0.6. The precursors were activated in the test unit with a 7.5% H₂/N₂ mixture for 1 hour at 418 to 493 K at a rate of 4 K/min.

Table 1: Chemical Composition and Physico-Chemical Properties of Fresh Catalysts

Catalysts	C ₃ Z ₆ A	C ₄ Z ₄ A ₂	C ₅ Z ₂ A ₃	CZA	CZ-A	CA-Z	Com-1
Comp., % wt Cu/Zn/Al	30/60/10	40/40/20	50/20/30	42/53/5	42/53/5	42/53/5	42/53/5
S _{BET} (m ² /g)	18.4	29.7	28.6	90.5	100.4	78.4	53.4
S _{Cu} ^a (m ² /g)	10.8	4.5	8.32	25.3	61.3	18.9	39.3
Dispersion ^b (%)	4.7	2.6	2.2	5.7	13.8	4.3	8.9

^a Copper surface area determined by N₂O chemisorption experiments

^b Ratio between amount of surface copper and total copper content

Physico - Chemical Characterization

Chemical analyses for Cu, Zn and Al were carried out on dried samples. Powder X-ray diffraction patterns were recorded on a Seifert diffractometer using nickel-filtered CuK α radiation ($\lambda = 0.1542$ nm). The BET surface area of the catalyst was calculated from the nitrogen adsorption isotherm at 77 K measured in a Micromeritics 2100 apparatus.

Chemisorption of nitrous oxide was measured in a Micromeritics 300 apparatus equipped with a TC detector. Typically, 0.3 g of the catalyst were reduced in 50 ml/min of 10% H₂/He. The catalyst sample was heated at 4 K/min to 493 K for 1 hour and then subjected to degassing at 353 K for 1 hour. Pulses of nitrous oxide diluted in a N₂ flow were allowed to flow through the catalyst at 353 K until no N₂O adsorption was detected. The amount of N₂O chemisorbed in each pulse could be calculated from the difference between the area of pulses when the surface is saturated and the area obtained in each pulse. For the calculation, it was assumed that the Cu/N₂O ratio was 2 and that the copper crystallography planes [100][111][110] were equally present in the

sample which produced a mean atomic surface area for copper of 7.41 \AA^2 (Evans et al., 1983). The temperature programmed reduction (TPR) experiments were carried out in an automatic Micromeritics 3000 apparatus interfaced to a data station. Since water is produced during reduction, the gas exiting from the reactor was passed through a cold trap before entering the thermal conductivity detector. The calcined sample (30 mg) was heated at 4 K/min from 290 K to 750 K in 80 ml/min of 10% H_2/N_2 .

Photoelectron spectra were acquired with a Fisons ESCALAB MkII 200R spectrometer equipped with a hemispherical electron analyzer and a MgK α 120 W X-ray source. A PDP 11/04 computer from Digital Equipment Co. was used for collecting and analyzing the spectra. The powder samples were pressed into small aluminum cylinders and then mounted on a sample rod placed in a pretreatment chamber and heated under vacuum at 373 K for 1 h prior to being moved into the analysis chamber. After analysis, the same catalyst sample was moved to the pretreatment chamber and reduced in situ by hydrogen at 493 K. The pressure in the ion-pumped analysis chamber was below 3×10^{-9} Torr (1 Torr = 133.33 N/m 2) during data acquisition. The spectra were collected for 20 to 90 min, depending on peak intensities, at a pass energy of 20 eV (1 eV = 1.602×10^{-19} J), which is typical of high resolution conditions. The intensities were estimated by calculating the integral of each peak after smoothing and subtracting the "S-shaped" background and fitting the experimental curve to a mixture of Lorentzian and Gaussian lines of variable proportions. All binding energies (BE) were referenced to the adventitious C 1s line at 284.9 eV. This reference gave BE values within an accuracy of ± 0.2 eV.

RESULTS AND DISCUSSION

X-Ray Diffraction

The X-ray diffraction patterns of calcined catalysts prepared by direct coprecipitation showed that all samples contained very well crystallized CuO, ZnO and Al $_2$ O $_3$ species, while all catalysts samples prepared by reverse coprecipitation contained poorly crystallized CuO, ZnO species. An additional poorly crystallized ($-\text{Al}_2\text{O}_3$ phase was detected. When alumina was added, the formation of surface copper spinel, where Cu $^{2+}$ ions were in a distorted octahedral environment, could be formed even at rather low calcination temperatures but no diffraction peaks of the spinel CuAl $_2$ O $_4$ were detected by XRD.

Bet Surface Area And Copper Surface Area

The BET surface areas, S_{BET} , of calcined catalysts are compiled in [Table 1](#). From these results, it is evident that the areas of the catalysts prepared by reverse coprecipitation were larger than the catalysts prepared by direct coprecipitation and the commercial catalysts. More specifically, the two-step-coprecipitated **CZ-A** catalyst area was higher than those for other two or three-step reverse coprecipitation counterparts. On the other hand, copper metal areas, S_{Cu} , as evaluated by N $_2$ O adsorption-decomposition on reduced samples, were larger for the two catalysts in which copper and zinc were simultaneously prepared by reverse coprecipitation (**CZ-A** and **CZA**). In particular, copper surface areas for the **CZA** and **CZ-A** catalysts were almost two and three times larger, respectively, than for the other two or three-step coprecipitated homologues.

The results indicate that copper dispersion was determined not only by the amount of copper in the catalyst. Different copper surface areas were obtained in catalysts containing the same amount of copper, solely by varying of the precursor salt precipitation sequence. This reflects the influence of the method of preparation on the nature of the copper phases formed and their interactions with the ZnO and Al $_2$ O $_3$ phases.

Catalytic Activity

In order to compare catalyst performance, the steam/gas molar ratio in the feed, overall pressure and contact time had to be maintained constant in the activity runs. Activity in the water gas-shift reaction was expressed as mmole of converted CO per hour and per kg of the catalysts (**C₃Z₆A**, **C₄Z₄A₂**, **C₅Z₂A₃** and **Com-1**) as a function of time (h), as displayed in [Figure 1](#). For these three catalysts, prepared by direct coprecipitation, the conversion of carbon monoxide was constant over time and lower than **Com-1**. We shall consider that the catalysts prepared by direct coprecipitation did not produce high dispersion surface copper and consequently show low activity.

The catalytic activity of the sample, prepared by reverse coprecipitation, in the water-gas shift reaction at low temperature was expressed as mmole of converted CO per hour and per kg of the catalysts (**CZA**, **CZ-A**, **CA-Z** and **Com-1**) as a function of temperature (K), as displayed in [Figure 2](#). According to this parameter, they could be broadly categorized in two groups: (i) **CZ-A** catalysts, obtained by simultaneous coprecipitation of copper and zinc and mixing with alumina that was precipitated separately, which show higher CO conversion, and (ii) **CZA CA-Z and Com-1** catalysts, exhibiting poorer catalytic performance. All the catalysts were totally selective for the low temperature shift reaction. The most active catalysts were the ones that presented the largest copper surface areas. These results show that there is a proportional relationship between catalytic activity and copper surface area (Robinson et al., 1990). Due to the small surface copper present in the catalysts prepared by the direct coprecipitation method and consequently the low catalytic activity, only the catalysts prepared by reverse coprecipitation were studied by other distinct techniques such as TPR and XPS.

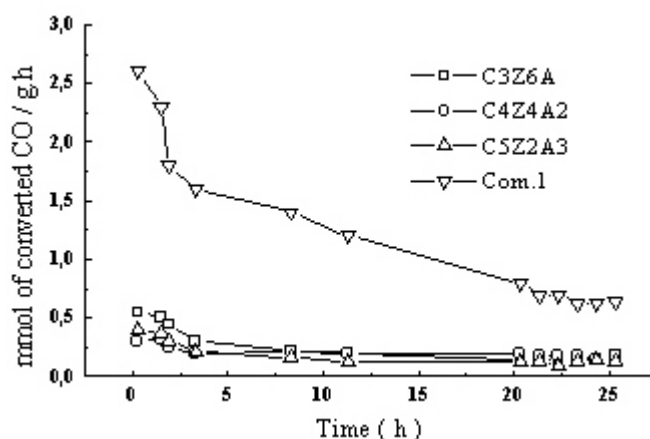


Figure 1: CO conversion rate for the catalysts, expressed as mmol of CO converted per Kg of catalysts per h as a function of time.

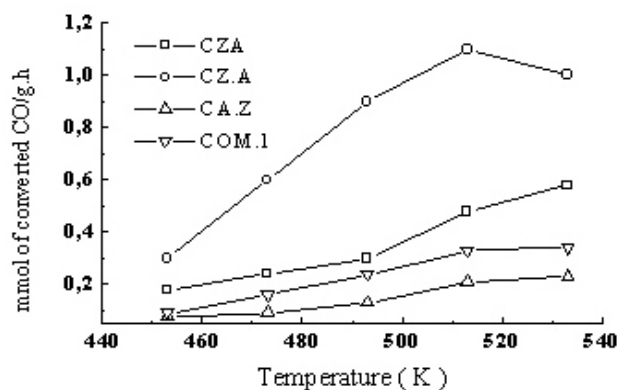


Figure 2: CO conversion rate for the catalysts, expressed as mmol of CO converted per Kg of catalysts per h as a function of reaction temperature.

Temperature - Programmed Reduction

Properties such as Cu^{2+} dispersion of Cu^{2+} on an oxide matrix, Cu^{2+} chemical environment, crystal size of CuO and degree of crystallization, among others, are key properties in determining reduction behavior. Therefore, TPR was a very valuable tool to detect alterations in the Cu^{2+} state in different samples. TPR profiles between 373 and 573 K are shown in [Figure 3](#). Estimation of the extent of reduction from the integral of these curves revealed that copper oxide was stoichiometrically reduced to Cu^0 .

The precursor reduction profiles presented in [Figure 3](#) show different profiles and peak positions. Considering that all the experiments were performed under the same conditions, such differences were caused by changes in the chemical environment. The distribution of metallic particle sizes in the catalysts and the reduction behavior of calcined samples were a consequence of the interaction between the Cu^{2+} , Zn^{2+} and Al^{2+} phases, of the dispersion of Cu^{2+} phases in the $\text{ZnO-Al}_2\text{O}_3$ matrix and CuO crystal size.

It is obvious from [Figure 3](#) that the main reduction process was composed of two steps. The reduction or H_2 -consumption corresponding to a shoulder peak at 350-425 K was mainly ascribable to a reduction of Cu^{2+} to Cu^{1+} , while the main reduction process was apparently attributable to the reduction of Cu^{2+} and/or Cu^{1+} to Cu^0 reducibles at 450-550 K. The broadened TPR spectra for the **CZA**, **CZ-A** and **CA-Z** catalysts indicate superpositions of two or three peaks. They can represent the indefinite structures of copper oxide in these catalysts. It is clearly demonstrated that, as temperature increases, at least four kinds of Cu^{2+} in the calcined $\text{CuO-ZnO-Al}_2\text{O}_3$ catalysts were reduced, and they were attributed to the copper in the ZnO lattice, in amorphous Cu oxide phases, in crystalline CuO and Cu^{2+} in the Al_2O_3 phase. Different profiles were obtained for each experiment. **CZA** reduction shows one peak and took place at 475 K similar to the **CA-Z** catalyst. The **CZ-A** catalyst shows a profile, which is different from the others. In addition to the main peak at lower temperatures (450-475 K), this catalyst presents a wider shoulder at 350-425 K and another shoulder at 500-550 K.

Surface Analysis By Xps

The oxidation state of catalyst components and their proportions at the surface were evaluated by photoelectron spectroscopy in both calcined and H_2 -reduced samples. The binding energy (BE) of the most abundant elements of all catalysts and pretreatment are summarized in [Table 2](#). BE of both Al 2s and Zn $2p_{3/2}$ peaks were essentially constant irrespective of sample pretreatment. [Figures 4](#) and [5](#) show the Cu $2p_{3/2}$ core-level of calcined and hydrogen-reduced samples, respectively. From these spectra it is evident that the line profile changes dramatically in hydrogen-reduced samples at 493 K. [Figure 4](#) displays the calcined sample principal Cu $2p_{3/2}$ peak somewhat above 934 eV, which is characteristic of Cu^{2+} ions in copper oxide. (Okamoto et al., 1984; Moretti et al., 1990). An additional means of identifying Cu^{2+} ions is the satellite peak, which is caused by electron shake-up processes. The origin of the satellite peaks is considered to be the promotion of 3d electrons to 4s and/or 4p levels or, alternatively, a charge transfer of ligand electrons to unfilled 3d. This transfer cannot occur in Cu^+ and Cu^0 because of their completely filled 3d shells. Peaks of calcined samples were deconvoluted into two contributions centered at around 933.5 eV and 935.1 eV, whose weight percentage corresponding to the area under each peak is tabulated in [Table 2](#). The peak at 935.1 eV is assigned to Cu^{2+} in the Al_2O_3 phase or in the CuAl_2O_4 spinel (Sepúlveda et al., 1993). No diffraction peaks of such spinel were detected in the XRD patterns, so the formation of both must be restricted at the surface. The peak at 933.5 eV is attributed to Cu^{2+} in the CuO phase or, at least, not in the spinel.

The relative changes in surface composition of the catalysts were also revealed by XPS. From the peak area, photoelectron cross-section and free path, the M/Zn (M = Cu, Al) atomic ratios were calculated. The atomic ratios of Cu/Zn and Al/Zn in the catalysts are summarized in [Table 2](#). According to the data in this table, changes in the percentage of surface aluminum were introduced by changing the preparation procedure. There is enrichment in Al at the surface, as suggested by the Al/Zn atomic ratio of calcined samples ([Table 2](#)). It must be taken into account that the Al/Zn theoretical bulk value is 0.09. This Al enrichment must be related to the penetration of Cu in the Al₂O₃ phase or forming the CuAl₂O₄ spinel at surface. It is clear that the Al/Zn and Cu/Zn ratios depend markedly on the method of preparation.

The weight percentage of surface aluminum changed with the kind of sample, and Cu²⁺ in the oxide matrix or in Al₂O₃ or CuAl₂O₄ was higher in **CZA** catalysts, as indicated by the higher weight percentage for such peaks and the higher Al/Zn atomic ratio (see [Table 2](#)). However, the catalytic activity in the water-gas shift reaction was not dependent on Al surface enrichment. The most active catalyst was **CZ-A**, which showed the largest dispersion of surface copper.

The disappearance of satellite peaks and the simultaneous shift of the principal Cu 2p_{3/2} peak towards lower BE upon H₂-reduction at 493 K are conclusive evidence that the copper species are Cu⁺ or Cu⁰, but in no case Cu²⁺. The strong decrease in the Cu/Zn ratios in H₂-reduced catalysts clearly indicates a lack of copper dispersion as a consequence of Cu particle formation in phases where Cu²⁺ was dispersed on an oxide matrix or in Al₂O₃ or CuAl₂O₄ spinel. The loss of dispersion during reduction appears to be related to the low Tammann temperature (T_M) of copper. Some copper dispersion takes place upon reoxidizing the metallic particles under carefully controlled conditions ([Figure 6](#)), as illustrated by the increase in the Cu/Zn intensity ratio in all the samples ([Table 2](#)) subjected to a complete reduction-oxidation cycle, but in no case was original copper exposure reached.

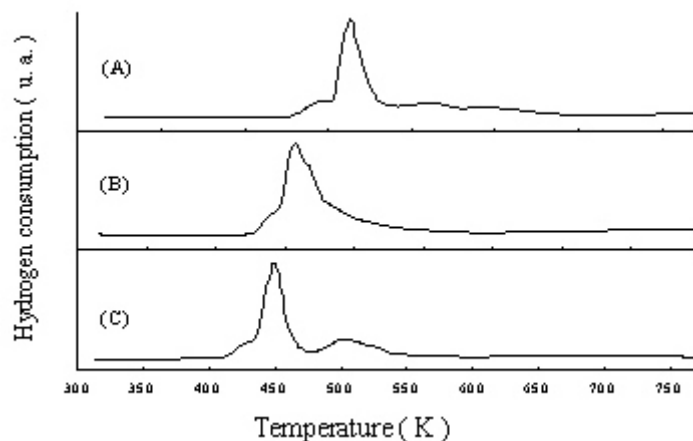


Figure 3: Temperature-programmed reduction (TPR) profiles of calcined samples (measured as H₂ consumption in a thermal conductivity detector): (a) CZA; (b) CZ-A; (c) CA-Z.

Table 2: Binding Energies (eV) of Core Electrons and Surface (XPS) Atomic Ratios of Catalysts Subjected to Reduction

Sample	Cu 2p _{3/2}	Zn 2p _{3/2}	Al 2s	Cu/Zn	Al/Zn
CZA, vac	932.9 (63) 935.0 (37)	1022.2	119.4	0.611	0.229
CZA, red	932.4	1022.2	119.5	0.449	0.237
CZA, reox	933.1 (81) 935.2 (19)	1022.2	119.4	0.509	0.201
CZ-A, vac	932.9 (83) 935.2 (17)	1022.2	119.4	0.724	0.177
CZ-A, red	932.4	1022.2	119.5	0.391	0.098
CZ-A, reox	933.0 (80) 935.0 (20)	1022.2	119.4	0.436	0.091
CA-Z, vac	932.9 (87) 934.9 (13)	1022.2	119.4	0.661	0.112
CA-Z, red	932.4	1022.2	119.5	0.386	0.089
CA-Z, reox	932.8 (86) 935.2 (14)	1022.2	119.4	0.569	0.105

vac - fresh catalyst

red - reduction in H₂ at 493 K for 1 h

reox - reoxidation at 673 K in air flow for 2 h

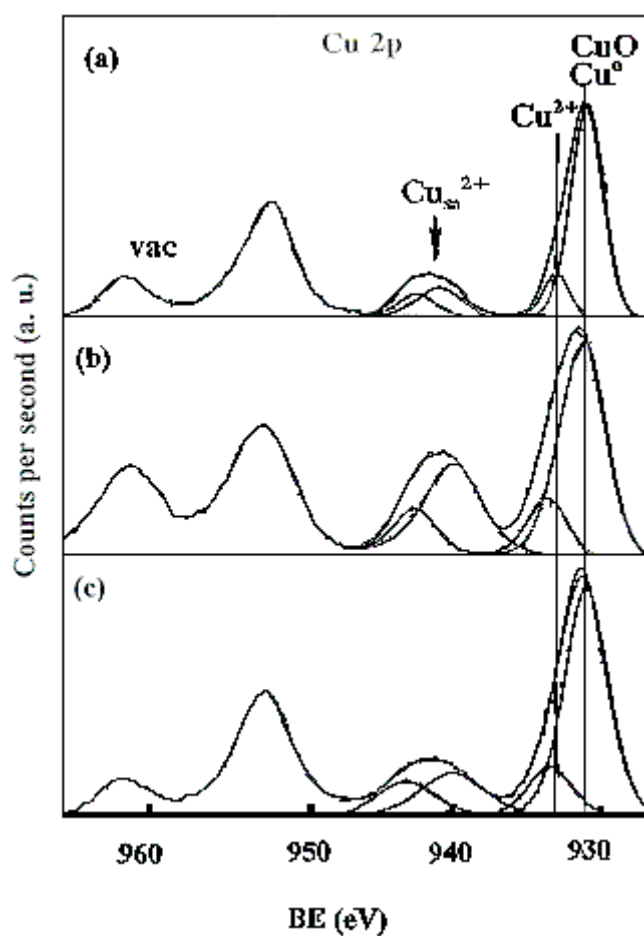


Figure 4: XPS Cu 2p core-level spectra of calcined samples outgassed at 298 K. (a) CZA; (b) CZ-A; (c) CA-Z.

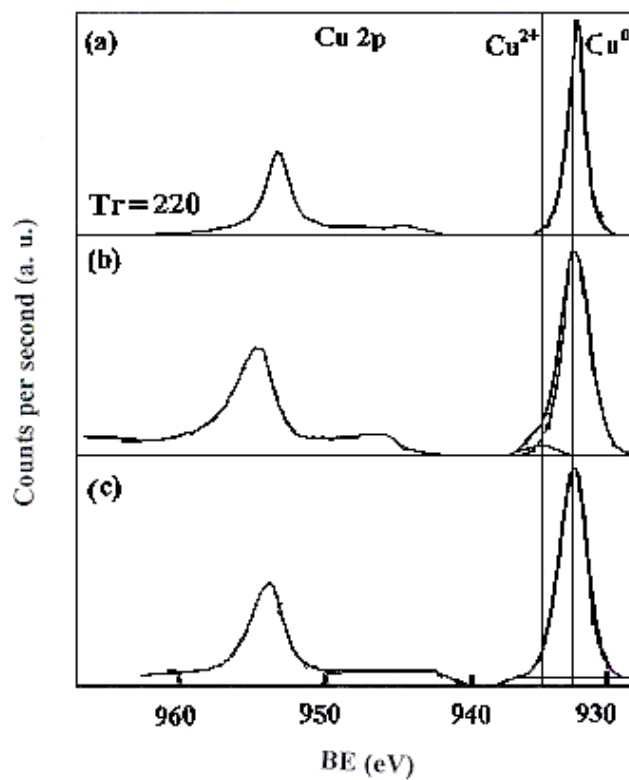


Figure 5: XPS Cu 2p core-level spectra of catalysts reduced in H₂ at 493 K. (a) CZA; (b) CZ-A; (c) CA-Z.

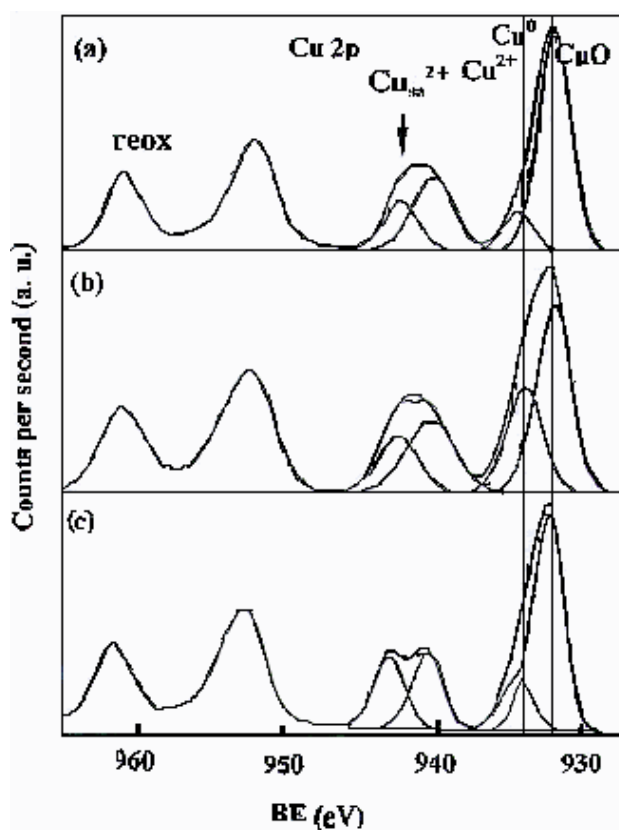


Figure 6: XPS Cu 2p core-level spectra of catalysts reoxidated at 673 K in air flow for 2 h. (a) CZA; (b) CZ-A; (c) CA-Z.

CONCLUSION

Changes in the sequence of coprecipitation of metal nitrates during the preparation of the precursor of Cu/ZnO/Al₂O₃ catalysts led to changes in the final properties of Cu⁰ at the surface of the catalysts. The interaction of Cu²⁺ with Zn²⁺ and Al²⁺ in the precursors seemed to determine the final state of Cu⁰. Copper surface areas varied. **CZ-A** and **CZA** precursors (those in which Cu nitrates and Zn nitrates were precipitated together) in resulted catalysts with the highest Cu surface area. CuAl₂O₄ spinel or Cu²⁺ dispersed on the Al₂O₃ matrix was detected by XPS at the surface of all the catalysts. **CZA** presented the highest concentration in such an environment. The development of copper in this environment was very likely related to the formation of samples with smaller Cu particles.

The **CZ-A** presented the highest catalytic activity. These results show that there is a proportional relation between catalytic activity and copper surface area.

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