

## Effect of Incorporation of $\text{Al}^{3+}$ Ion on the Structure of Cu-Zn Coprecipitate

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Ternary catalysts containing oxides of copper, zinc, and aluminum have been widely used as catalysts for water-gas shift reactions and methanol synthesis. Although many studies have been carried out with the calcined mixed oxides, very little information is available regarding the effect of  $\text{Al}^{3+}$  on the structure of the copper-zinc hydroxycarbonate which is the precursor of the catalyst. On the basis of the findings of the present investigation it has been suggested that  $\text{Al}^{3+}$  partially replaces  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions in the aurichalcite structure during coprecipitation, and this process of replacement causes appreciable changes in X-ray and electron diffraction patterns, infrared spectra, and the thermal stability of the precursor. These changes occur due to distortion of the aurichalcite structure of the coprecipitate by  $\text{Al}^{3+}$ , which has a higher charge and a stronger acid character than  $\text{Cu}^{2+}$  or  $\text{Zn}^{2+}$  ions. © 1995 Academic Press, Inc.

### INTRODUCTION

Ternary catalysts having the composition Cu/Zn/Al are well-known active catalysts for low-pressure methanol synthesis and low-temperature water-gas shift reactions. These types of catalysts with various compositions and prepared by different techniques have been studied extensively by different workers (1-10). These studies dealt with the effect of  $\text{Al}^{3+}$  incorporation on the stability and activity of the CuO-ZnO catalyst. It has been reported (7) that addition of  $\text{Al}^{3+}$  widens the Cu/Zn compositional range which can be used to produce an active catalyst. This is a result of increased dispersion of Cu and ZnO occurring in the Al-containing catalyst in the active state. According to Petrini *et al.* (10), the presence of Al promotes the dissolution of  $\text{Cu}^+$  in the ZnO matrix and higher concentrations of the Al phase can act as an antisintering agent.

It is obvious that in order to understand the role of  $\text{Al}^{3+}$  incorporation it is necessary to obtain the coprecipitate of Cu, Zn, and Al in a well-defined single-phase form, in

which case the extent of mutual interaction is expected to reach its maximum. In the literatures cited above, only Refs. (9), (10), and (11) have discussed the structure of the coprecipitated ternary catalyst precursor on the basis of X-ray and thermal analysis data. In a coprecipitate having an approximate composition of Cu:Zn:Al of 30:60:10,  $\text{Al}^{3+}$  ion may form a separate phase with a structure similar to that of hydrotalcite or scarbroite, or the three metal ions may together form a single phase of unknown structure. In view of this it seems necessary to study the problem using different techniques for better understanding of the structure of the coprecipitate.

### EXPERIMENTAL

Samples containing Cu, Zn, and Al were prepared by coprecipitation from mixed metal nitrate solutions with ammonium bicarbonate at a pH of 6.8-7.0 and temperatures from 323 to 333 K under controlled conditions of atmosphere and stay time of the precipitate. Concentrations of metal nitrate and ammonium bicarbonate solutions were kept at 0.1 M and the metal nitrate solutions were mixed in a requisite proportion so that each sample contained 30% CuO by weight and varying amounts of ZnO and  $\text{Al}_2\text{O}_3$  for the balance. The coprecipitates were dried for 12 hr in air at 333 K and finally cured at 623 K for 5 hr. The cured samples were chemically analyzed to determine the percentage of Cu, Zn, and Al. The samples were denoted  $A_0$ ,  $A_2$ ,  $A_6$ ,  $A_{10}$ , and  $A_{15}$ , where the subscript indicates the percentage of  $\text{Al}_2\text{O}_3$  by weight. Details of the sample preparation are reported elsewhere (12). An X-ray investigation of the dried precipitates and cured samples was carried out with a Philips X-ray diffractometer using  $\text{CuK}\alpha$  radiation, the scanning speed being maintained at 0.5° per minute. A Perkin-Elmer Model 421 IR grating spectrometer and a Siemens Elmiskop 1A were used for infrared spectroscopy and electron microscopy of the dried samples. For studying the decomposition pattern of the samples during curing a Stanton Redcroft Model TG 750 thermogravimetric balance was used.

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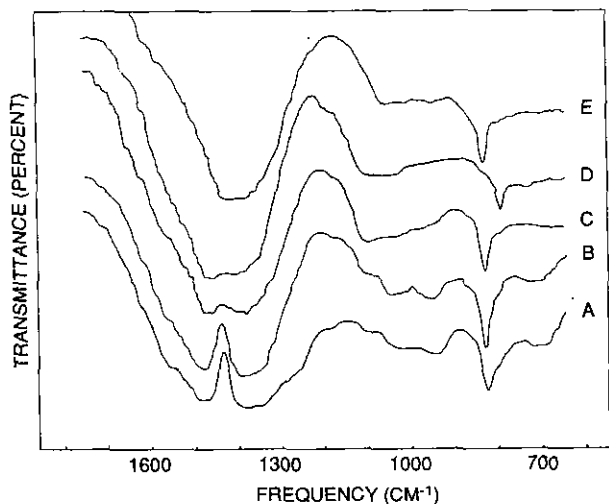


FIG. 1. Infrared spectra of Cu-Zn-Al coprecipitates. (A)  $A_0$ , (B)  $A_2$ , (C)  $A_6$ , (D)  $A_{10}$ , and (E)  $A_{15}$ .

## RESULTS AND DISCUSSION

### X-Ray Diffraction

The X-ray study reveals that the structure of the dried sample  $A_0$  is similar to that of aurichalcite,  $(\text{Cu}, \text{Zn})_5$

$(\text{CO}_3)_2(\text{OH})_6$ , which can be derived from the structure of hydrozincite. According to Ghosh (13), hydrozincite has the  $C_6$ -type structure of  $\text{Zn}(\text{OH})_2$ , in which one-quarter of the  $\text{Zn}^{2+}$  ions are removed from the octahedral sheet and one-quarter of the  $\text{OH}^-$  ions are replaced by  $\text{O}^{2-}$  so that the resulting  $\text{Zn}_3(\text{OH})_6(\text{O}^{2-})_2$  sheet becomes negatively charged. To satisfy that charge, tetrahedral  $\text{Zn}^{2+}$  ions and  $\text{CO}_3^{2-}$  groups occur above and below the missing  $\text{Zn}^{2+}$  ions, one oxygen atom of the  $\text{CO}_3^{2-}$  group being a part of the  $\text{Zn}_3(\text{OH})_6(\text{O}^{2-})_2$  sheet. In the case of aurichalcite,  $\text{Cu}^{2+}$  ions preferably occupy the octahedral sites, imparting a blue color to the dried coprecipitate (14). For  $\text{Al}^{3+}$ -containing samples Gherardi *et al.* (9) have reported the presence of a hydrotalcite-like phase  $(\text{Cu}, \text{Zn})_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$  for all compositions, but in the present investigation no such phase could be detected even for samples  $A_{15}$ . On the other hand, with increasing percentages of  $\text{Al}^{3+}$ , the particle size of the aurichalcite phase decreases monotonically and the distribution of cations becomes random, as indicated by the diffuse nature of characteristic X-ray lines. For samples  $A_{15}$  the aurichalcite lattice breaks down and the X-ray pattern shows the amorphous nature of the sample. These observations indicate that  $\text{Al}^{3+}$  ions have been incorporated

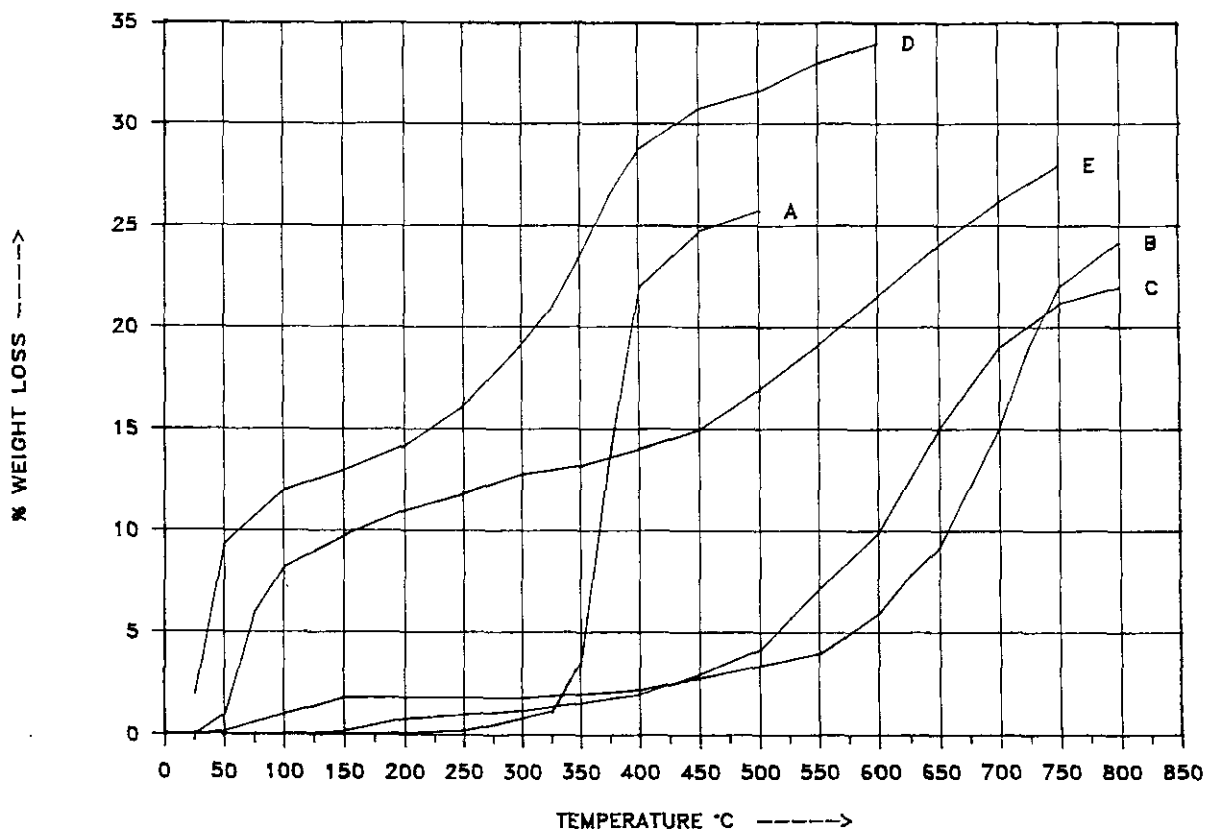


FIG. 2. TGA thermograph of Cu-Zn-Al coprecipitates. (A)  $A_0$ , (B)  $A_2$ , (C)  $A_6$ , (D)  $A_{10}$ , and (E)  $A_{15}$ .

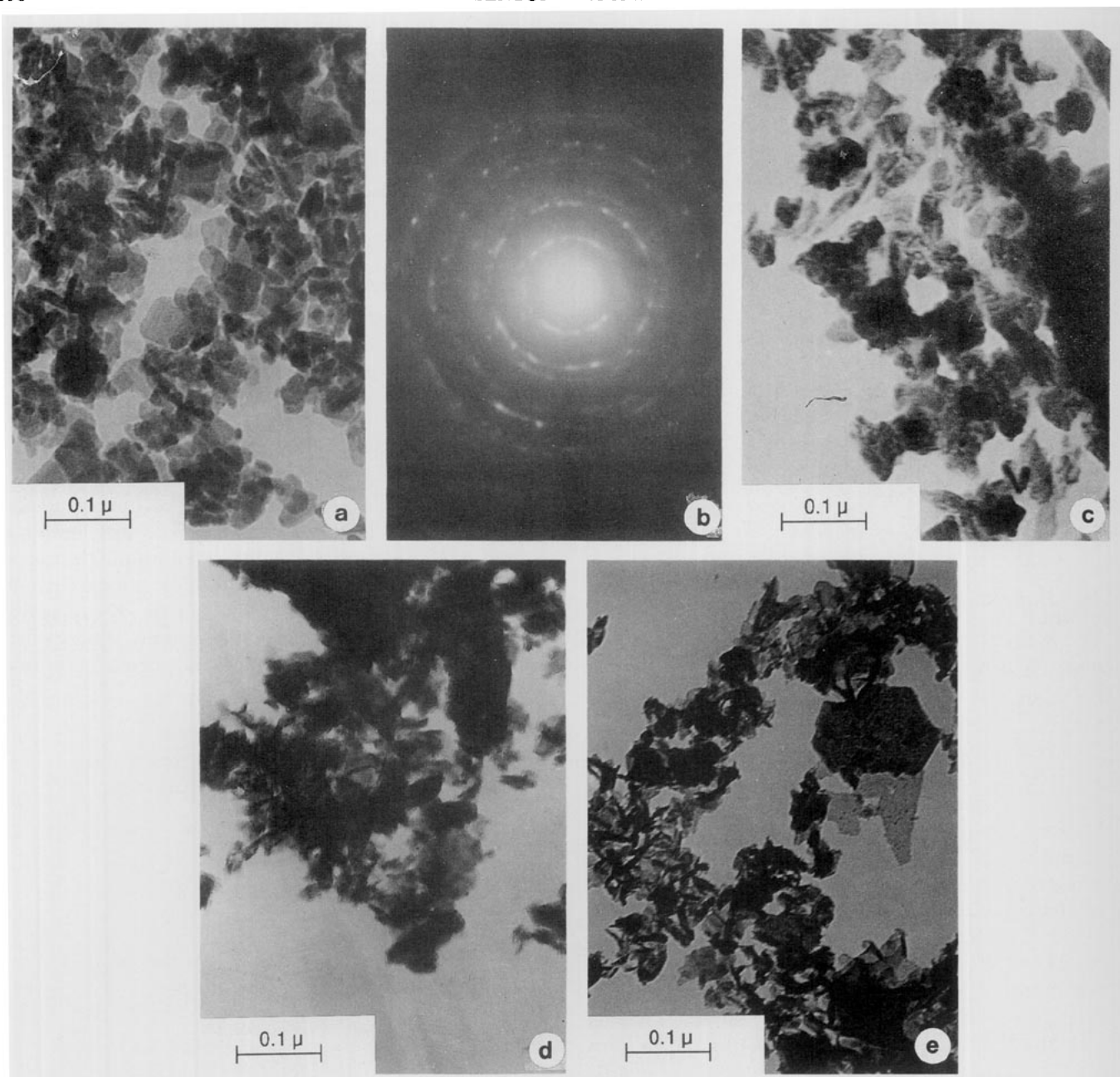


FIG. 3. Electron micrograph and diffraction pattern of Cu-Zn-Al coprecipitates. (a, b)  $A_0$ , (c)  $A_2$ , (d)  $A_6$ , and (e)  $A_{10}$ .

into the aurichalcite structure, causing distortion. The smaller ionic radii of the  $\text{Al}^{3+}$  ion ( $0.57 \text{ \AA}$ ) compared to those of the  $\text{Cu}^{2+}$  ( $0.72 \text{ \AA}$ ) and  $\text{Zn}^{2+}$  ( $0.83 \text{ \AA}$ ) ions can make such incorporation possible.

#### IR Spectra

The IR spectra of the dried sample  $A_0$  presented in Fig. 1 show a doublet in the  $1400\text{--}1370 \text{ cm}^{-1}$  range, a feature characteristic of basic carbonates, and two more absorption bands at  $840$  and  $700 \text{ cm}^{-1}$ . With increasing  $\text{Al}^{3+}$  content the doublet becomes less well defined and

broadens out, and finally for  $A_{15}$  a single broad peak at  $1400 \text{ cm}^{-1}$  is obtained.

In aurichalcite the  $\text{CO}_3^{2-}$  groups lie normal to the zinc sheets and are covalently bonded to  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions through two oxygen atoms, whereas the third oxygen atom is hydrogen bonded to three OH groups. This makes the three oxygen atoms nonequivalent and causes the splitting of the stretching frequency in the  $1480\text{--}1370 \text{ cm}^{-1}$  range. However, according to Allmann (16) the  $\text{CO}_3^{2-}$  ions in hydrotalcite lie horizontally between the  $\text{Al}(\text{OH})_3$  sheets and behave more or less as free ions. The apprecia-

ble ionic character of the bond between the CO<sub>3</sub><sup>2-</sup> and Al<sup>3+</sup> ions is due to the higher charge and acid character of the aqueous Al<sup>3+</sup> ion compared to Cu<sup>2+</sup> or Zn<sup>2+</sup> ions. Therefore if some of the Cu<sup>2+</sup> or Zn<sup>2+</sup> ions in aurichalcite are replaced by Al<sup>3+</sup>, an increasing number of CO<sub>3</sub><sup>2-</sup> ions behave as free ions and the doublet character of the absorption band in the 1480–1370 cm<sup>-1</sup> range gradually changes into a broad one, indicating a transition from a covalent to an ionic type of bonding of CO<sub>3</sub><sup>2-</sup> ions with metal ions.

### Thermal Analysis

From the results of the thermogravimetric analysis in Fig. 2 it can be seen that in the case of sample A<sub>0</sub> there is a sharp weight loss between 590 and 673 K with slow and small changes above and below this temperature range. But with increasing Al<sup>3+</sup> content the change becomes less pronounced and broad, covering a wider temperature change from 425 to 673 K. The structure of mixed copper zinc hydroxycarbonate is such that each metal atom is in square-planar or near-square-planar coordination with oxygen atoms belonging to the OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup> groups. Herman *et al.* (4) have visualized the decomposition of hydroxycarbonate as a condensation of CO<sub>3</sub><sup>2-</sup> groups with two protons from the nearest OH<sup>-</sup> groups which results in the simultaneous release of both H<sub>2</sub>O and CO<sub>2</sub>. Incorporation of Al<sup>3+</sup> disrupts this ordered arrangement and consequently the condensation reaction is gradually replaced by the simple decomposition of OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup> groups so that CO<sub>2</sub> and H<sub>2</sub>O are formed independently. The observed broadening of the thermogravimetric peak can, therefore, be due to overlapping of separate evolution peaks of CO<sub>2</sub> and H<sub>2</sub>O. Moreover samples A<sub>10</sub> and A<sub>15</sub> show appreciable weight loss at about 273 K which is due to liberation of free moisture. When these samples are dried at 393 K for 12 hr and then exposed to air at room temperature, reversible adsorption of water vapor takes place, which indicates the presence of finely dispersed Al(OH)<sub>3</sub> on the surface of these samples.

### TEM Study

The micrographs and selected-area diffraction patterns of all the samples are presented in Fig. 3. The electron micrograph (Fig. 3a) of sample A<sub>0</sub> shows an opaque darker phase along with a transparent flaky constituent. The diffraction pattern of the dark opaque phase (Fig. 3b) shows a doublet around  $d_{hkl} = 4.57 \text{ \AA}$ , and lines (410) and (600) corresponding to this doublet are characteristic lines of aurichalcite. These are weak lines and are therefore not observed in the XRD. The electron micrograph of sample A<sub>2</sub> (Fig. 3c) shows opaque aurichalcite grains, each grain consisting of a cluster of minute crystallites measuring

around 80 Å. Figure 3d shows that sample A<sub>6</sub> consists of the aurichalcite phase together with thin elongated crystallites. The population of the needle-like crystallites increases with increasing Al<sup>3+</sup> content as can be seen from Fig. 3c. Electron diffraction studies show that the needle-like crystals are zinc oxide supported on hexagonal flakes of Al<sub>2</sub>O<sub>3</sub>. Moreover the size of the aurichalcite grains decreases with increasing Al<sup>3+</sup> content as can be seen by comparing Figs. 3a, 3c, and 3d, the micrographs of A<sub>0</sub>, A<sub>2</sub>, and A<sub>6</sub>, respectively. Finally, Fig. 3e shows that in sample A<sub>10</sub> the aurichalcite phase has disintegrated and free zinc oxide and copper oxide are seen to be present in large amounts. However, the crystallite size of these metal oxides is too small to be detected by XRD.

### CONCLUSION

The results of the present investigation show that during coprecipitation of the mixed hydroxycarbonates from a solution containing Cu, Zn, and Al nitrates, Al<sup>3+</sup> ions are incorporated in the aurichalcite structure. Due to the higher charge and stronger acid nature of aqueous Al<sup>3+</sup> ions compared to that of Cu<sup>2+</sup> and Zn<sup>2+</sup> ions, the aurichalcite structure of the coprecipitate is distorted, causing changes in the X-ray diffraction pattern, IR spectra, and the thermal decomposition process of the coprecipitate.

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