Mechanism of the formation of precursors for the Cu / ZnO methanol synthesis catalysts by a coprecipitation method

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Precursors of Cu/ZnO catalysts with various Cu/Zn molar ratios were prepared by a coprecipitation method. It was found that amorphous copper hydroxycarbonate and sodium zinc carbonate were intermediates for the formation of various precursors such as hydrozincite, malachite and aurichalcite. Aurichalcite having a high Cu/Zn ratio was prepared from a mechanical mixture of these intermediates.

Keywords: precursors of Cu/ZnO catalysts; coprecipitation; preparation of aurichalcite

1. Introduction

For preparation of active supported metal catalysts, the metal components are generally required to be dispersed in the precursors of the catalysts at molecular levels. Coprecipitation of the ingredients of the catalysts is frequently employed for this purpose. Much work has been carried out on the characterization of coprecipitated binary Cu/ZnO catalysts [1–10], since these catalysts exhibit high performances for the methanol synthesis and the water–gas shift reaction [11–16].

For the binary system, coprecipitated precursors consisted of hydrozincite, $Zn_5(CO_3)_2(OH)_6$, aurichalcite, $(Cu_x, Zn_{1-x})_5(CO_3)_2(OH)_6$, malachite, $Cu_2(CO_3)(OH)_2$, rosasite, $(Cu_x, Zn_{1-x})_2(CO_3)(OH)_2$, or their mixtures [1–10]. The structures of the precursors varied by the Cu/Zn molar ratio, the preparation method employed and the conditions of the preparation.

A monophasic precursor of aurichalcite having a Cu/Zn molar ratio of 30/70 has been prepared by coprecipitation methods [4,6,10]. Monophasic aurichalcite with a Cu/Zn molar ratio of 50/50 was obtained from a solution of metal nitrates and that of Na_2CO_3 by Stacey and Shannon [5]. However, details of the preparation were not described.

Himelfarb et al. pointed out that a single phase precursor of aurichalcite gave rise to a high activity of Cu/ZnO for the methanol synthesis [4]. Therefore more active catalysts may be obtained from aurichalcite containing higher content of copper.

In the present study, the precursors of Cu/ZnO catalysts with various Cu/Zn molar ratios ranging from 0/100 to 100/0 were prepared from copper and zinc nitrates and $NaHCO_3$ by a coprecipitation method similar to that employed by Porta et al. [7]. We showed that amorphous copper hydroxycarbonate and sodium zinc carbonate, $Na_2Zn_3(CO_3)_4 3H_2O$, formed in the preparation of the catalyst played pivotal roles in the formation of the precursors, such as hydrozincite, malachite and aurichalcite. A monophasic presursor of aurichalcite having a high Cu/Zn ratio was prepared from a mechanical mixture of the amorphous copper hydroxycarbonate and sodium zinc carbonate.

2. Experimental

Precursors of Cu/ZnO catalysts with various Cu/Zn molar ratios in a range of 0/100 to 100/0 were prepared by a coprecipitation method. 50 cm^3 of a 1 M solution of copper and zinc nitrates was added dropwise to 100 cm^3 of a 1.2 M solution of $NaHCO_3$ ($pH = 8.2$) over a period of 20 min at 338 K under continuous stirring. The precipitates formed were further aged for 90 min under stirring at the same temperature. The precipitates were then filtered out, washed with distilled water and dried at 373 K overnight.

The precursors prepared were analyzed by X-ray diffraction (XRD), differential thermal analysis (DTA), thermal gravimetric analysis (TGA), UV/VIS spectroscopy and diffuse reflectance FT-IR spectroscopy. In some of the runs, the precipitates were collected from the solution for their characterization during the addition of a mixed solution of the nitrates or during the aging.

DTA and TGA were carried out in air at a heating rate of 10 K/min. Some samples of the precipitates were decomposed in a He flow and gases evolved were analyzed by gas chromatography. Amounts of the precursors in the precipitates were determined on the basis of the integrated intensities of the XRD peaks or DTA peaks of the mechanically mixed authentic samples in variable ratios.

3. Results and discussion

Fig. 1 shows the effect of Cu/Zn ratio upon the composition of the precipitates obtained after the aging [10]. The composition of the precipitates is practically in good agreement with that prepared by Porta et al., although they prepared the catalysts with high Cu/Zn ratios [7].

The structure of the precipitates was followed in time during the addition of the

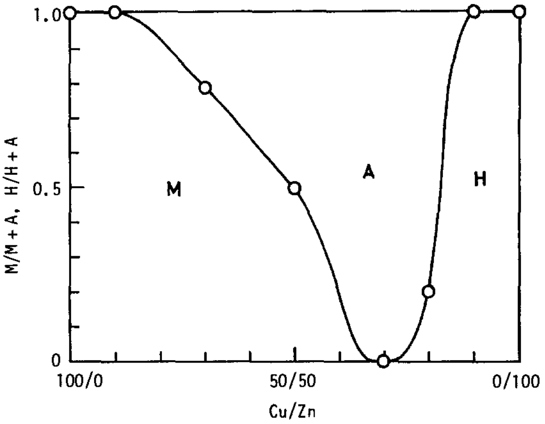

Fig. 1. Variation of the composition of precipitates with Cu/Zn ratio. M, H and A represent malachite, hydrozincite and aurichalcite, respectively. The composition was in molar fraction.

nitrates and the aging. Fig. 2 illustrates the variation of the XRD patterns of pure zinc precipitates sampled from the solution during the addition of the zinc nitrate and during the aging. The precipitates formed in the initial stage of the addition show the characteristic pattern of sodium zinc carbonate [17]. The peaks ascribed to sodium zinc carbonate decrease in intensity with time and the peaks ascribed to

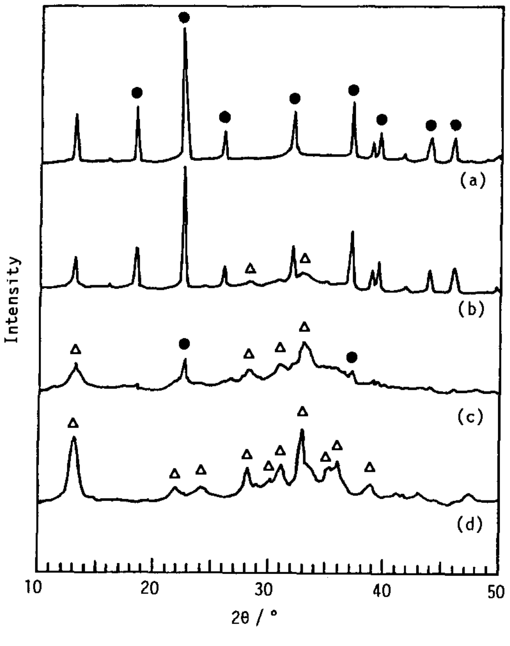

Fig. 2. Variation of the XRD patterns of pure zinc precipitates with time. The precipitates were sampled after (a) 4 min, (b) 12 min, (c) 18 min and (d) 25 min.

hydrozincite [18] appear. The peaks for hydrozincite were sharpened to some extent after aging for 90 min. Therefore, we concluded that zinc nitrate was converted into hydrozincite through the formation of sodium zinc carbonate.

When a solution of copper nitrate was added to the solution of $NaHCO_3$, the precipitates formed were initially amorphous as revealed by the XRD method. After the aging for 5 min, the structure of the precipitates changed. The characteristic pattern of malachite [19] appeared in a XRD spectrum.

In the IR spectrum of the amorphous precipitates, strong absorptions occurred at 3430, 1480, 1370 and 835 cm^{-1}, indicating that the species having hydroxyl and carbonate were formed. When the amorphous precipitates were heated in a helium flow, the precipitates decomposed to CuO, giving CO_2 and H_2O. These features in the XRD pattern, the IR spectrum and in the thermal decomposition of the amorphous precipitates were quite similar to those of georgeite reported by Polland et al. [20]. This suggested that the amorphous precipitates were hydroxycarbonates. Hence, we concluded that copper nitrate was converted into malachite through the formation of the amorphous hydroxycarbonates.

Similar experiments were carried out for the preparation of the precursors having Cu/Zn molar ratios of 30/70, 50/50 and 70/30. The precursor species initially formed exhibited XRD peaks ascribed to sodium zinc carbonate. No copper-containing species was detected by XRD. However, the precipitates showed a strong absorption at 800 nm in the UV/VIS spectra, suggesting that copper-containing precursors were formed in addition to sodium zinc carbonate, and the structure of copper-containing precursors was amorphous. As shown earlier, the copper-containing precipitates formed were most probably present as the amorphous hydroxycarbonate.

Fig. 3 illustrates the variation of the relative content of the precipitates, which

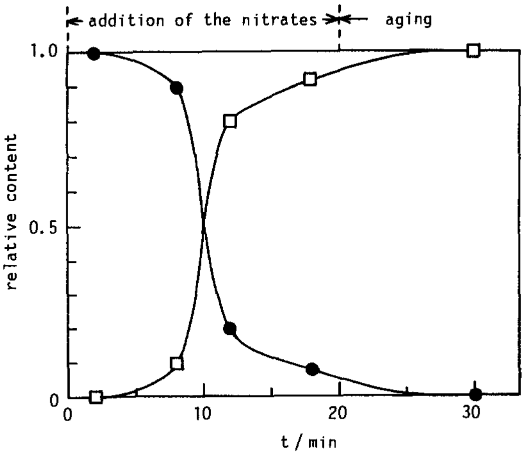

Fig. 3. Variation of the relative content of the precipitates with time in the preparation of the precursors with Cu/Zn ratio of 30/70. (●) Sodium zinc carbonate; (□) aurichalcite.

was determined on the basis of the XRD spectra, in the preparation of the precursor with the Cu/Zn ratio of 30/70. It shows that sodium zinc carbonate initially formed decreases gradually with time and aurichalcite [21] increases.

Similar experiments were carried out for the precipitates formed at Cu/Zn ratios of 50/50 and 70/30. Sodium zinc carbonate was also produced along with copper-containing amorphous precipitates at the initial period of the preparation. However, in contrast to the results for the precipitates with Cu/Zn ratio of 30/70, the XRD peaks ascribed to malachite and aurichalcite increased at the expense of those ascribed to sodium zinc carbonate. Fig. 4 depicts the variation of the relative content of the precursors determined by the XRD method for the precipitates formed at the Cu/Zn ratio of 50/50 with time. The relative content for malachite varies with time in a similar manner to those for aurichalcite. This suggests that these species are formed through a parallel pathway.

A mechanical mixture of the amorphous precipitates and sodium zinc carbonate separately prepared (Cu/Zn = 50/50) was allowed to stand in a 1.2 or 0.1 M solution of $NaHCO_3$ at 338 K. Fig. 5 shows the XRD patterns of the product thus obtained. The structure of the products depends markedly upon the concentration of the $NaHCO_3$ solution. In the 1.2 M solution of $NaHCO_3$, the mechanical mixture is converted into a mixture of aurichalcite and malachite. By contrast, aurichalcite is selectively formed from the mechanical mixture in the 0.1 M solution.

Similar experiments were carried out for the mechanical mixtures of various precipitates. The results obtained are summarized in table 1. It is clear that aurichalcite is formed only in the presence of sodium zinc carbonate and the amorphous hydroxycarbonate. When malachite is used instead of the amorphous precipitates, sodium zinc carbonate is merely transformed to hydrozincite. No aurichalcite was

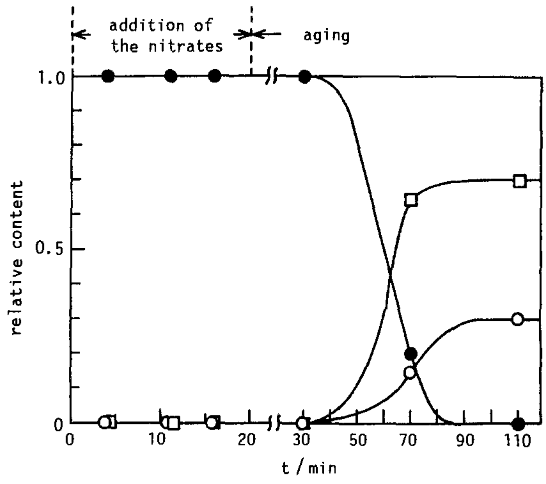

Fig. 4. Variation of the relative content of the precipitates with time in the preparation of the precursors with Cu/Zn ratio of 50/50. (●) Sodium zinc carbonate; (□), aurichalcite; (○) malachite.

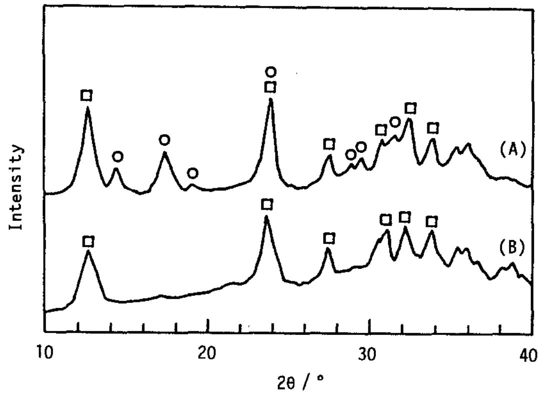

Fig. 5. XRD patterns of the precipitates obtained from the mixture of the amorphous copper hydroxycarbonate and sodium zinc carbonate in the $NaHCO_3$ solution. The concentration of the $NaHCO_3$ solution was (A) 1.2 M and (B) 0.1 M. (□) Aurichalcite; (○) malachite.

detected by XRD and DTA methods. Similar to this, when hydrozincite is used in place of sodium zinc carbonate, the amorphous precipitate is converted into malachite. The hydrozincite remains unchanged. No reaction occurs when malachite, aurichalcite or hydrozincite alone is added to the $NaHCO_3$ solutions.

When a solution of copper nitrate was added to various concentrations of the $NaHCO_3$ solutions, malachite was produced at different rates. In the 1.2 M $NaHCO_3$ solution, malachite was formed at the first 5 min of the aging. In the 0.1 M $NaHCO_3$ solution, it was slowly formed. XRD peaks for malachite were discerned after 17 min of the aging. As previously discussed [10], the transformation of the amorphous copper hydroxycarbonate to malachite proceeded most probably

Table 1
Structure changes of various precipitates in a $NaHCO_3$ solution [a]

Reactant [b]	Final structure of precipitates
Am + SZC (Cu/Zn = 50/50)	M + A A [c]
Am + SZC (Cu/Zn = 30/70)	A
M + SZC	M + H
Am + H	M + H
M + H	M + H
A	A
M	M
SZC	H
Am	M

[a] Precipitates prepared were added to a 1.2 M $NaHCO_3$ solution.

[b] Am, amorphous copper hydroxycarbonate; SZC, sodium zinc carbonate; A, aurichalcite; M, malachite; H, hydrozincite.

[c] The concentration of the $NaHCO_3$ solution was 0.1 M.

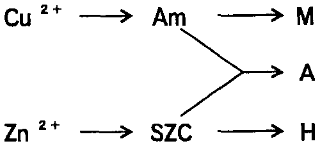

Fig. 6. A scheme for the formation of the precursors. Am, amorphous copper hydroxycarbonate; SZC, sodium zinc carbonate; M, malachite; A, aurichalcite; H, hydrozincite.

through the exchange of hydroxide ions of the amorphous copper hydroxycarbonate with carbonate ions in the solution. On the basis of this mechanism of the malachite formation, it was suggested that the amorphous precipitates were slowly attacked by carbonate ions for the mixture of the amorphous precipitates and sodium zinc carbonate in lower concentrations of $NaHCO_3$. Under such conditions, the amorphous precipitates were probably attacked by sodium zinc carbonate in preference to carbonate ions, being converted into aurichalcite in high selectivity. On the other hand, in higher concentrations of $NaHCO_3$, the amorphous precipitates were preferentially transformed to malachite because of the rapid rate of the exchange between hydroxide ions in the precipitates and carbonate ions in the solution.

Based on these results, we concluded that the amorphous copper hydroxycarbonate competitively reacted with carbonate ions or sodium zinc carbonate, being transformed to malachite or aurichalcite (fig. 6).

In closing, it is to be noted that aurichalcite was selectively produced in lower concentration of the $NaHCO_3$ solution from the mechanical mixture of the amorphous copper precipitates and sodium zinc carbonate separately prepared. Through this process aurichalcite having a high Cu/Zn molar ratio (Cu/Zn = 50/50) was obtained. A Cu/ZnO catalyst prepared from this precursor species was more active than that prepared from malachite alone or a mixture of malachite and aurichalcite for the methanol synthesis from CO_2 and the steam reforming of methanol [22]. Details of the results will be reported in the near future.

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