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Precursors of copper/zinc oxide catalysts

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Recent results on hydroxycarbonate precursors of copper/zinc oxide catalysts for methanol synthesis are reinterpreted, taking into account earlier work on these systems.

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1. Introduction

Catalysts containing copper metal and zinc oxide are widely used for hydrogenation and dehydrogenation reactions. Methanol synthesis and the water–gas shift reaction are important examples. Commercial catalysts for these processes normally contain one or more additional, refractory oxides (e.g., Al_2O_3, Cr_2O_3, MgO, ZrO_2) to give greater stability but zinc oxide is of primary importance in making and maintaining a good dispersion of copper metal crystallites. Most of the many published studies of the precursors of these catalysts have been of the simple copper/zinc binary system rather than the three- or four-component systems. As part of a recent paper on the effects of zinc oxide on methanol synthesis catalysts, Fujitani and Nakamura [1] examined the role of hydroxycarbonate precursors in obtaining Cu/ZnO catalysts of high activity. They concluded that “methanol is mainly produced over the catalyst prepared from aurichalcite”, i.e., zincian-aurichalcite. It is shown here that Fujitani and Nakamura have ignored the experimental evidence of the formation of zincian-malachite in their own results. Further they have also ignored much previous work [2–15] on the various hydroxycarbonate precursors of methanol synthesis catalysts, especially the initial formation of georgeite and the subsequent importance of zincian-malachite in the preparation of catalysts of high activity.

2. Results of Fujitani and Nakamura

Fujitani and Nakamura [1] prepared various Cu/ZnO catalysts with the final weight compositions from 0 to 100 wt% ZnO, at 10 wt% intervals. They used a continuous coprecipitation method of the type used industrially [2,3] and by many other workers [4–16]. The catalyst precursors, after ageing, washing, filtering and drying, but before calcination, were examined by X-ray diffraction to determine the phases present. These were found (see figure 6 in [1]) to be malachite, aurichalcite and hydrozincite. Four compositions gave single phase products:

0% ZnO – malachite,

10% ZnO – zincian-malachite,

40% ZnO – zincian-aurichalcite,

100% ZnO – hydrozincite.

In their subsequent interpretation Fujitani and Nakamura [1] ignore the formation of the 10% zincian-malachite and refer to zincian-aurichalcite as the only zincian copper hydroxycarbonate. It is not clear why they do this. With the limited, single technique used, Fujitani and Nakamura [1] were unable to determine the elemental compositions of the different phases in the biphasic (20 and 30% ZnO, 50–90% ZnO) systems. A comparison with prior work suggests that the compositions of the separate phases in these mixtures could be close to those of the single phases. In an earlier, more detailed study of the same system Porta et al. [4,5] found a single zincian-malachite phase up to 15% ZnO. At higher zinc concentrations, up to 50% ZnO, the zinc content of the malachite phase continued to increase but a second phase of zincian-aurichalcite also appeared in increasing amounts. Closely similar results were obtained by Stone and Waller [16]. Waller et al. [8] showed that the initial precursor obtained in the system with 33% ZnO consisted of two distinct phases. X-ray diffraction, IR spectroscopy, electron diffraction and other experimental techniques proved that the zincian-malachite phase in the precursor contained 15% ZnO and the zincian-aurichalcite phase, about 40% ZnO. After ageing the precursor was found to be only zincian-malachite containing 33% ZnO. Thus the experimental results of Fujitani and Nakamura [1] are consistent with those of earlier workers but do not add any new information.

3. Ageing of catalyst precursors

In the production of commercial copper/zinc oxide catalysts a period of ageing of the wet precipitate is essential for the formation of active catalysts. Fujitani and Nakamura [1] used a period of ageing ("… 48 h with stirring at room temperature …") in their catalyst preparations but did not consider the changes in composition of the catalyst precursor before, during or after ageing. However, these changes are of great significance in the development of maximum catalytic activity. The consecutive phase changes during ageing of a 2 : 1 Cu/Zn mixture are given in figure 1. The beneficial result of ageing is the production of finely crystalline zincian-malachite in which the zinc and copper cations are uniformly distributed in the crystal structure: this gives the optimum distribution of copper metal on the zinc oxide support in the final catalyst. Similar sequences occur in the preparation of catalysts with other Cu/Zn ratios.

The initial product of precipitation at all Cu/Zn ratios from 100 : 0 to 50 : 50 is georgeite, a blue copper hydroxycarbonate, $Cu_2CO_3(OH)_2$, containing zinc, i.e., zinciangeorgeite. Several groups of workers [4,5,11,12,18], preparing precipitates over a wide range of compositions, had described a change in colour from blue of the initial precipitate to a green or blue-green of the aged material. Clearly the colour of the aged material corresponded well to the malachite or malachite/aurichalcite mixtures but the initial blue colour indicated a different phase. This was identified by Pollard et al. [15] as zincian-georgeite. Georgeite is a mineral of low stability in contact with the mother liquor, although zincian-georgeites are more stable than pure copper georgeite [15]. The subsequent conversions in ageing, first to malachite/aurichalcite mixtures and then by recrystallisation to malachite alone, were examined in detail by Waller et al. [8]. The recent results of Fujitani and Nakamura [1] are in agreement with the earlier work, although they ignore the initial formation of georgeite and the ageing of their precipitates did not continue to the conversion of zincian-aurichalcite to zincian-malachite.

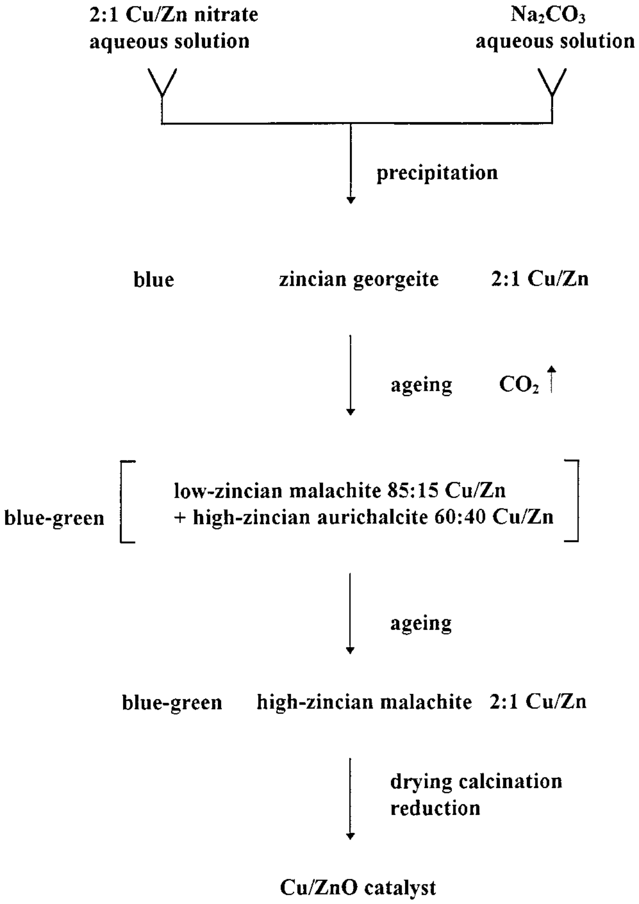

Figure 1. Reaction scheme for the precipitation, ageing and subsequent stages in the preparation of 2 : 1 Cu/Zn catalysts [15,17].

The times required for the transitions in ageing are strongly dependent on precipitation and ageing conditions, as is shown in the comparison of the results of Fujitani and Nakamura [1] and other workers in table 2. These results from different groups of workers are not directly comparable because of differences in conditions and methods, but some general conclusions can be drawn. At 60 °C the con-

Table 1
Phase analyses of copper–zinc hydroxycarbonates prepared by coprecipitation.

ZnO (wt%)	Phases present[a]					
	Porta et al.[b]			Fujitani and Nakamura[c]		
	M	A	H	M	A	H
0	100	0	0	100	0	0
8	100	0	0	–	–	–
10	–	–	–	100	0	0
15	100	0	0	–	–	–
20	–	–	–	95	5	0
23	90	10	0	–	–	–
30	–	–	–	60	40	0
33	60	40	0	–	–	–
40	–	–	–	2	98	0
50	10	80	10	0	85	15

[a] Phases present: M – malachite, A – aurichalcite, H – hydrozincite.
[b] DTA and XRD results from table 1 in [4].
[c] DTA results from figure 6 in [1].

Table 2
Comparison of copper–zinc hydroxycarbonate phases formed in ageing after coprecipitation of Cu/Zn mixtures.

Cu/Zn atom ratio	Ageing time (min)	Temperature (°C)	pH	Phases present[a]	Reference
3.3	<1	60	[b]	G	[15]
3.3	<1	25	[b]	G	[15]
2.3	20.2×10^3	20	[b]	G	[15]
2.0	ca. 1	60	7.0	0.15M, 0.40A	[8]
2.0	30	60	7.0	0.33M	[8]
2.0	205	60	7.0	0.33M	[8]
2.0	95–200	60–70	ca. 8.0[b]	0.3M, A	[4]
2.0	2.92×10^3	Ambient	6.8–7.0	M, A	[1]

[a] Phases present: G – georgeite, M – malachite, A – aurichalcite, 0.15M – malachite with Cu/Zn = 85/15, etc. When two phases present, major component listed first.
[b] Reverse coprecipitation, pH not constant. All other preparations, continuous coprecipitation, giving constant pH.

version of zincian-georgeite is fast, as is the subsequent conversion of zincian-aurichalcite, but these reactions are several orders of magnitude slower at ambient temperature. Thus the failure of Fujitani and Nakamura [1] to reach a substantial conversion of aurichalcite to malachite can be attributed to their choice of precipitation and ageing at ambient temperature. The full conversion of aurichalcite to malachite was reached only by Waller et al. [8], working close to the conditions used for the manufacture of commercial copper/zinc oxide catalysts.

4. Catalyst activities

In any correlation of catalyst activities of copper catalysts with the catalyst precursors a distinction has to be made between effects on copper metal surface area and on the catalyst specific activity. The precipitation conditions and type of precursor can influence the nature of the working catalyst in both respects. The copper–zinc hydroxycarbonate phase from the ageing stage is dried, calcined and then reduced to give the final catalyst. These stages in the conversion of an aurichalcite precursor have been examined in detail in studies by Couves et al. [13] and Sankar et al. [14], relevant work ignored by Fujitani and Nakamura [1]. The local environment and electronic state of the Cu^{2+} ions remained unchanged, even when at ca. 450 °C the material was converted to a mixture of CuO and ZnO.

The water–gas shift reaction over Cu/ZnO catalysts has been shown [19,20] to be a “structure-sensitive” reaction, i.e., the specific catalytic activity of the copper surface is a function of catalyst composition and preparation. Hadden et al. [20] identified the importance of the hydroxycarbonate precursor and ageing conditions in determining specific activity. In contrast, methanol synthesis over Cu/ZnO catalysts is essentially a “structure-insensitive” reaction [19]. Linear relations between methanol synthesis activity and copper metal surface area have been widely observed, e.g., [19,21], and also found by Fujitani and Nakamura [1] (their figure 3). Burch et al. [22] showed that the results by several groups of workers with a variety of Cu/ZnO-containing catalysts indicated a near-constant specific activity. It follows that the effects of precursors on catalyst activity in methanol synthesis are almost solely in terms of the copper metal surface area generated in the reduced catalyst and not in variations of specific activity.

Fujitani and Nakamura [1] compared (their table 1) the yields of methanol from synthesis over catalysts made from malachite, aurichalcite and hydrozincite precursors. They concluded: “This clearly indicates the methanol production activity depends not on the Cu/ZnO weight ratio but on the aurichalcite precursor. That is, methanol is mainly produced over the catalyst prepared from aurichalcite”. This conclusion is not valid. They compare the activity of three catalysts, derived from pure copper malachite, from 60Cu/40ZnO aurichalcite and from pure zinc hydrozincite. The activity of the catalyst derived from aurichalcite was much more active than the other two catalysts. These results demonstrate not that active catalysts are formed only from aurichalcite but simply the well-known fact that both copper and zinc are required for active catalysts. A comparison with their 90Cu/10ZnO malachite catalyst could have given more meaningful results, as indeed would a comparison with earlier results cited above.

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