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Catalysts for Low-Temperature Methanol Synthesis. I. A Study of the Reduction Process

O. RUGGERI, F. TRIFIRÒ, AND A. VACCARI

Facoltà di Chimica Industriale, Università di Bologna, Viale del Risorgimento, 4, 40136 Bologna, Italy

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A study of the reduction of CuO in a ternary oxide system (Cu : Zn : Al, atomic ratio 62 : 14 : 24) demonstrated that at lower temperatures it occurred in two stages, whereas at higher temperatures it was no longer possible to display the formation of Cu_2O. The rate of reduction of CuO was strongly reduced on decreasing the partial pressure of hydrogen, while the presence of CO_2 stabilized the Cu_2O, delaying the reduction to copper. On the basis of simpler systems it was possible to demonstrate the activating effect of Al_2O_3 and the delaying effect of ZnO on the reduction of CuO.

Introduction

Cu–Zn–Al ternary oxide systems are known to be active catalysts at low temperatures for the CO conversion reaction and for the synthesis of methanol (*1–5*). These catalysts are directly activated in the reactor via a reduction process (*6*). This reaction involves the reduction of CuO to metallic copper, since the reduction of any brass containing ZnO takes place at temperatures higher than those generally employed. While papers dealing with the reduction of pure CuO are numerous (*7–8*), we have little information about the copper oxide that is dispersed and/or associated with other elements, particularly the oxides of zinc and aluminum.

The aim of our research was to identify the factors that regulate the reduction of a CuO–ZnO–Al_2O_3 system and the stability of any intermediates. A study of the reduction of this ternary system could lead to a determination of the role of the ZnO and Al_2O_3 and of any changes in the structure of the CuO by a comparison with the behavior of simpler systems, such as pure CuO, CuO–ZnO, and CuO–Al_2O_3.

Experimental

The precursor (Cu : Zn : Al with an atomic ratio of 62 : 14 : 24) was obtained by precipitation from a solution containing the dissolved nitrate salts of the elements with a slight excess of $NaHCO_3$ at 60°C with energetic agitation. The precipitate was suspended in CO_2-saturated distilled water and kept at 90°C overnight with stirring. The subsequent filtration was performed, followed by washing with CO_2-saturated distilled water until the sodium concentration, determined with a Mark II E.E.L. flame photometer, was less than 0.05% (as Na_2O). The drying temperature was 90°C.

X-Ray analysis of the precursor thus obtained showed the presence of malachite, modified for the presence of zinc, and amorphous alumina. The precursor was calcined in air for 20 hr at 250°C, resulting

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in the oxides of the respective metals, reduced to a powder, and crushed to a particle size of 0.125–0.250 mm. To better understand the roles of the individual components of the ternary precursor, the following samples were prepared analogously: $CuO-Al_2O_3$ (atomic ratio 72:28), $CuO-ZnO$ (atomic ratio 82:18), and CuO.

The reduction reactions were performed in a Cahn RG thermobalance choosing a weighing sensitivity of 10 μg and a heating rate of 5°C/min.

The precursors in powder form were placed in vertically suspended quartz crucibles. All trials were performed on 2- to 4-mg samples so as to limit any delaying effects due to diffusion phenomena and/or the formation of thermal gradients in the solid that could affect the overall process, in agreement with (*9*). In addition, also with the aim of improving the reproducibility of the trials and to avoid even small procedural differences affecting the reactivity, the trials were performed on samples derived from a single preparation.

All samples were conditioned at the reduction temperature for 2 hr in a nitrogen flow before introduction of the reduction mixture. The reduction trials, performed isothermally, were run in the 155–255°C range using gaseous mixtures of hydrogen in nitrogen at 150 kPa (1.2 liters/hr flow rate) at different hydrogen concentrations and, in some cases, also in the presence of carbon dioxide.

Under the experimental conditions employed, according to Ref. (*6*), only CuO was reduced. The curves of the reduction processes were obtained by plotting, according to Refs. (*9, 10*), the fraction of CuO reduced (i.e., the fraction of oxygen removed from the CuO, analogously to that reported by Kawasaki *et al.* for iron oxide (*11*)) against the time.

X-Ray powder diffraction data were obtained with a Philips X-ray unit using a 114.6-mm Debye camera with nickel-filtered Cu$K\bar{\alpha}$ radiation ($\lambda = 0.154178$ nm). Samples were sealed in 0.5-mm capillary tubes under dry nitrogen and exposed to X rays for a mean time of 4 hr. *d*-Spacings were evaluated from the 4θ (Cu$K\bar{\alpha}$) measured with an optical device; the line intensities were estimated visually. Both *d*-spacings and line intensities were used to identify the compounds that contributed to the diffraction patterns. All crystalline phases were identified, but no Al_2O_3 was detected as a separate phase because of its low concentration and X-ray-amorphous state. In some cases, powder patterns were obtained from a Philips diffractometer by a counting method. Different crystal sizes and perfection were evident from the different line broadenings and, for the more crystalline compounds, the X-ray data permitted an accurate determination of the unit cell parameters by a least-squares fit of the observed interplanar spacings of the individual reflections. Crystal sizes were measured from the half-width of the reflections, using the Sherrer formula with $K = 1$. The observed half-width B was corrected from the instrumental broadening b, using the relation $\beta = (B^2 - b^2)^{1/2}$. Where unit cell parameters were calculated, no significant deviations from those usually reported in the literature were found. In particular, a value of 0.3615 nm (*1*) was consistently found for the side of the elementary cell of copper. This value corresponds to pure crystalline copper (NBS-1953) and indicates that no partial ZnO reduction occurred (e.g., a brass containing 13% Zn gave a value of 0.3624 nm (*1*)).

Results and Discussion

In the presence of H_2–N_2 (2:98 v/v) the ternary precursor reduced, starting at 155°C (Fig. 1a). At this temperature the reduction rate decreased with time monotonically. At 165 and 175°C the reduction occurred according to two sigmoid curves,

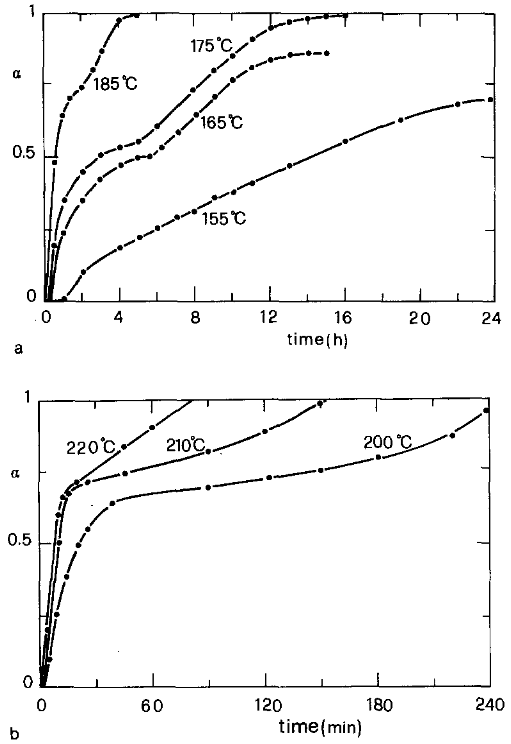

FIG. 1. TG curves for the reductions of the CuO–ZnO–Al_2O_3 system with H_2–N_2 (2:98 v/v) for the range from 155 to 185°C (a) and the range from 200 to 220°C (b).

both characterized by an induction time. The first *S* curve ended at approximately 50% reduction at 165°C after 5 hr and at 175°C after 4 hr, whereas the second *S* curve reached 80 and 98% in 14 hr (at 165 and 175°C, respectively).

At 185°C we observed one curve with an inflection point and with a lower and upper portion (the first ended with a reduction of about 75% after 2 hr and the second reached 100% in 4 hr), whereas an induction time was no longer seen.

At higher temperatures (Fig. 1b) the reaction was very rapid and ended in short times that ranged from 4 hr (200°C) to 80 min (220°C). It was no longer possible to identify distinct reduction behaviors.

When we reduced the hydrogen concentration to 0.7% the reaction followed a monotonic curve (Fig. 2, curve a); the induction time was about 25 min and the reduction reached 50% only after 34 hr. Figure 2 also shows the curves for the reduction processes of the ternary precursor with a mixture of H_2–CO_2–N_2 (1.6:0.8:97.6 v/v). Up to about 40–50% reduction the kinetics of the processes were qualitatively similar to those obtained with the 2% hydrogen mixtures, after which percentage the carbon dioxide notably delayed the reduction. In fact, total reduction was reached only after 40 hr of treatment at 175°C and 18 hr at 185°C (Fig. 2, curves b and c).

In Fig. 3, we show the reduction curves for CuO, CuO–Al_2O_3, and CuO–ZnO systems. One can see that the reductions were complete and that all occurred with monotonic curves, with high initial reduction rates, which progressively decreased in time.

On the basis of the illustrated results one can identify, for particular temperatures and hydrogen concentrations, three distinct stages in the reduction process of the ternary precursor (Fig. 1a). The first, a period of induction, is attributable to a "germination" process (*9*, *10*). Since the quantity of transformed material was very small, reli-

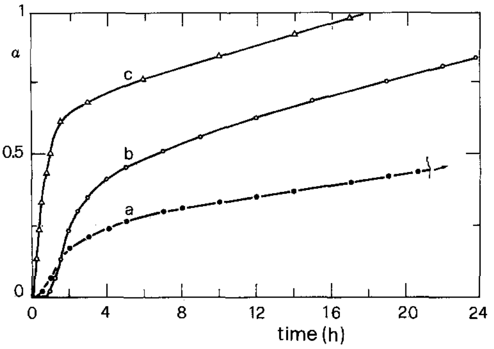

FIG. 2. TG curves for the reductions of the CuO–ZnO–Al_2O_3 system at 175°C with H_2–N_2 (0.7:99.3 v/v) (curve a); at 175°C with H_2–CO_2–N_2 (1.6:0.8:97.6 v/v) (curve b); and at 185°C with H_2–CO_2–N_2 (1.6:0.8:97.6 v/v) (curve c).

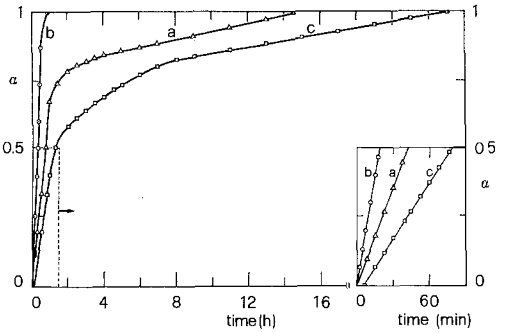

FIG. 3. TG curves for the reduction at 245°C of the CuO (curve a), CuO–Al_2O_3 (curve b), and CuO–ZnO (curve c) systems with H_2–N_2 (0.7 : 99.3 v/v).

able identification of the chemical nature of these early crystalline seeds was difficult, even though the X-ray data for the partially reduced samples demonstrated the presence of small quantities of copper, present as small crystallites, along with CuO and Cu_2O (Fig. 4). The second stage ended with 50% reduction of the total CuO. The X-ray analysis of the partially reduced samples demonstrated the presence of Cu_2O along with the small quantities of copper mentioned above (Fig. 5). Under these conditions, therefore, the reduction took place via the stabile intermediate Cu_2O. The third stage leads to the formation of metallic copper and has a sigmoid curve similar to that of the second stage, with an induction time that can be localized at an α of ca. 0.5. At higher temperatures (200–220°C) the reduction proceeded very rapidly and led directly to metallic copper, whereas an induction time was no longer observable. At lower temperatures the reduction was delayed, and the germination phase required 60 min at 155°C and 15 min at 175°C. The hydrogen concentration in the mixture greatly affected the curve of the reduction (Fig. 1a and Fig. 2, curve a), which was considerably delayed as the concentration was decreased, with a notable increase in the induction time as well. The presence of carbon dioxide, even in small concentrations, in the gaseous mixture stabilized the copper (I), delaying the reduction, in agreement with Herman *et al.* (*12*), who found the formation of the Cu^+/ZnO in the presence of carbon dioxide, and the direct formation of copper in its absence.

In Table 1, the values of the dimensions of the CuO crystals, alone or in the binary and ternary oxides, are reported. We used independently the lines ($\bar{1}11$) and (111) of CuO to avoid the superposition effect of the lines (002) and (200), respectively. Where possible, also the ($\bar{2}02$) line was used. The values reported are the averages of the different results. Our procedure for the CuO–Al_2O_3 system led to the formation of smaller crystals than those of the CuO, with a superficial dispersion that can be attributed to the amorphous state of the Al_2O_3 particles, like that observed for the CuO–SiO_2 system by Robertson *et al.* (*13*).

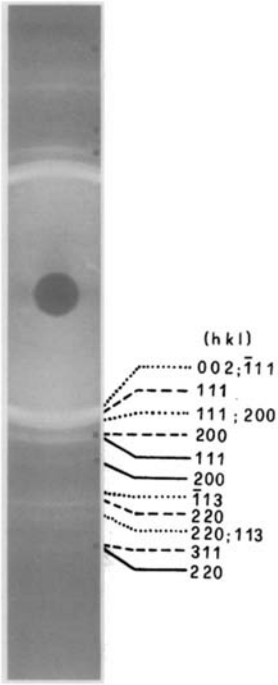

FIG. 4. X-Ray powder photograph of the ternary sample examined after the early stage of the reduction. It is possible to observe broad and very weak lines of metallic copper (——, marked also with a dot) together with those of Cu_2O (– – –) and CuO (· · ·).

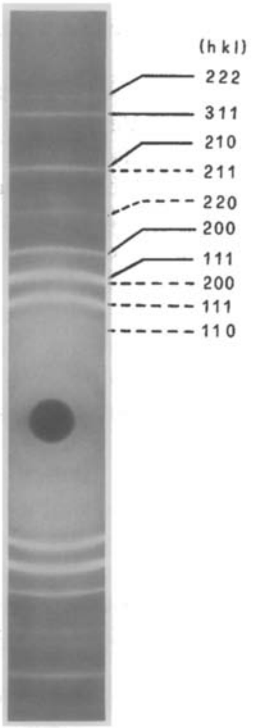

FIG. 5. X-Ray powder photograph of the ternary sample examined before the last stage of reduction. The diffraction lines of Cu_2O (---) and Cu (——) are the only ones present.

This dispersion enhances the reactivity of CuO oxide toward reduction (Fig. 3, curves a and b).

On the other hand, the CuO–ZnO system, although demonstrating small crystals, showed a slower reduction rate (Fig. 3, curve c). It is therefore necessary in this case to assume the existence of an interaction between the two oxides with the probable formation of a solid solution (*10*), which has a greater resistance to reduction.

The ternary $CuO-ZnO-Al_2O_3$ system had small crystals and a good reducibility, even though it showed a slower reduction rate as compared to $CuO-Al_2O_3$. In this case, therefore, in addition to the activating action associated with Al_2O_3, there is present, even though reduced, the interaction of ZnO with the CuO. The persistence of the latter interaction is, on the other hand, demonstrated by the existence, under particular reaction conditions, of the stable intermediate copper (I), which was never observed for the zinc-free systems.

TABLE I

AVERAGE SIZE OF CuO CRYSTALS FOR PURE, BINARY, AND TERNARY SYSTEMS

Sample	Average size of CuO crystals (nm)
CuO	14.0 ± 0.5
$CuO-Al_2O_3$	10.5 ± 0.5
CuO–ZnO	7.5 ± 0.5
$CuO-ZnO-Al_2O_3$	7.5 ± 0.5

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