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Behaviour of Cu(II) hydroxide during mechanical treatment

V. Blaskov, D.D. Radev* and D. Klissurski
Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113 (Bulgaria)

N.D. Yordanov
Institute of Kinetics and Catalysis, Bulgarian Academy of Sciences, Sofia 1113 (Bulgaria)

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Abstract

It has been established that Cu(II) hydroxide ($Cu(OH)_2$) can be decomposed mechanochemically to CuO. After dry grinding, $Cu(OH)_2$ is dehydrated for 3 h, while wet grinding (in a cyclohexane medium) for the same period of time cannot ensure that the decomposition process will be completed. During mechanical treatment, the samples are activated, which is confirmed by the broadening of the X-ray lines, the decrease in the temperature of thermal decomposition of $Cu(OH)_2$, and the appearance of additional exothermic peaks on the differential thermal analysis curve. The CuO obtained by mechanochemical decomposition is reduced more easily than CuO produced by thermal decomposition of $Cu(OH)_2$, regardless of the fact that $Cu(OH)_2$ has a larger specific surface area.

1. Introduction

Cu(II) oxide (CuO) participates in the formation of a series of inorganic materials, such as catalysts, for the following: (1) CO conversion; (2) nitrogen oxide oxidation; (3) cyclohexanol dehydrogenation etc., as well as for ferrites and composite materials for electronics. In many cases, CuO should possess a defect structure and a higher reactivity (*e.g.* when used in heterogeneous catalysis, in solid state reactions, etc. Such oxides can be obtained by the methods of mechanochemistry. Investigations on the mechanochemical decomposition of metal hydroxides and oxyhydroxides have mainly concentrated on the system FeOOH–Fe_2O_3 [1–7]. However, it is of interest to investigate the behaviour of other systems subjected to mechanochemical treatment. Here, we have studied the mechanochemical decomposition of Cu(II) hydroxide ($Cu(OH)_2$), on which there is no information in the available literature.

2. Experimental details

A solution of NH_4OH was added at 343 K to a 1 M solution of $CuSO_4 \cdot 5H_2O$, which led to the formation of a Cu–NH_3 complex. This complex was decomposed by the addition of 2M, NaOH, forming $Cu(OH)_2$. The $Cu(OH)_2$ was subjected to mechanical treatment in a Fritsch planetary mill using a stainless steel bowl and balls. The total mass of the balls was 200 g. The duration of the mechanical treatment was 3 h. The mechanochemical decomposition was achieved in two ways: by dry grinding (denoted as method A) and wet grinding (method B). The wet grinding was carried out under cyclohexane. The sample weight in both cases was 10 g and the solid-to liquid ratio was 1:1.

IR spectra were obtained using KBr pellets. The X-ray spectra were recorded with Cu Kα radiation. The thermal analysis was performed with a heating rate of 10 °C min^{-1}. The reduction of the oxides was carried out in static circulation apparatus. The electron spin resonance (ESR) spectra were recorded on Bruker ER 200 DSRC equipment. The specific surface area was measured using a modified Brunauer–Emmett–Teller (BET) method [8].

3. Results and discussion

It has been established by IR spectroscopy and X-ray phase analysis that $Cu(OH)_2$ contains no other copper phases. It has also been found that, after coming in contact with cyclohexane, $Cu(OH)_2$ shows no phase changes.

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*Author to whom correspondence should be addressed.

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The IR and X-ray data indicate that mechanical treatment is accompanied by dehydration of $Cu(OH)_2$ to CuO. According to the IR data, the initial $Cu(OH)_2$ is weakly carbonized (there are peaks at 1380 and 1510 cm^{-1}) and contains a small amount of adsorbed water, indicated by a peak at 1630 cm^{-1} (Fig. 1, curve A). These bands exist also after the completion of the mechanochemical decomposition process. We believe that this is a result of the enhanced adsorption ability of CuO formed during the grinding. Thus, Isupova *et al.* [9] have found that, during mechanical treatment, CuO adsorbs CO_2 and H_2O from the ambient air. As the process of mechanochemical decomposition progresses, the bands at 415, 690 and 935 cm^{-1} characteristic of $Cu(OH)_2$ (Fig. 1, curve A) disappear and the configuration of three peaks at 450, 520 and 595 cm^{-1} (which are characteristic of CuO) is formed, with the most intense peak being at 520 cm^{-1} (Fig. 1, curves B–E). At 400–1000 cm^{-1}, the IR spectrum of the sample prepared by wet grinding contains several bands belonging to the not completely decomposed $Cu(OH)_2$ – at 510, 640, 690 and 935 cm^{-1} (Fig. 1, curve D). The spectrum of the sample obtained by dry grinding exhibits only one peak of $Cu(OH)_2$ at 690 cm^{-1} (Fig. 1, curve B). After 3 h of dry grinding, the $Cu(OH)_2$ is completely dehydrated (Fig. 1, curve C), whereas some $Cu(OH)_2$ remains not completely decomposed after a similar period of wet grinding (Fig. 1, curve E).

The X-ray data also show a more rapid dehydration of $Cu(OH)_2$ after dry grinding (Fig. 2, curves A–D). From the X-ray patterns, it is evident that the peaks for CuO obtained by method A are broadened and less intense in comparison with the peaks for CuO obtained by method B. This is especially clear when comparing the reflections belonging to 020, $\bar{2}02$ and 110 faces of the CuO (Figs. 2, curves A, B and D). This result can be explained by the more defective structure of CuO obtained by dry grinding. This and the data on the faster mechanochemical decomposition show that dry grinding is more efficient than wet grinding.

The differential thermal analysis (DTA) curve of $Cu(OH)_2$ presents only one effect (endothermic) which is associated with the thermal dehydration of the hydroxide (Fig. 3, curve A). At the beginning of the mechanical treatment by method A, a shift of the minimum in the endothermic effect E_M to lower temperatures is observed. For the sample obtained after 10 min of dry grinding, E_M is established at 423 K (Fig. 3, curve B); in contrast, for the initial $Cu(OH)_2$ specimen, E_M is found at 463 K (Fig. 3, curve A). These results indicate that, at the beginning of dry grinding, the $Cu(OH)_2$ is activated. The same shift is also observed after wet grinding; however, this is only

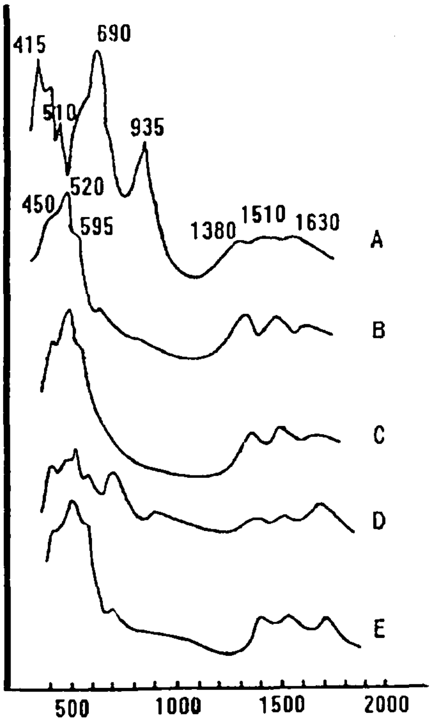

Fig. 1. IR spectra of (A) initial $Cu(OH)_2$, and samples obtained after (B) 1 h of dry grinding, (C) 3 h of dry grinding, (D) 1 h of wet grinding and (E) 3 h of wet grinding.

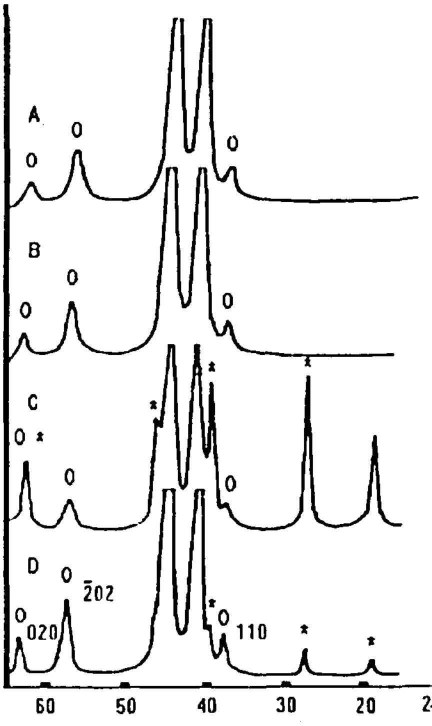

Fig. 2. X-ray patterns of samples obtained after (A) 1 h of dry grinding, (B) 3 h of dry grinding, (C) 1 h of wet grinding and (D) 3 h of wet grinding: *, $Cu(OH)_2$; O, CuO.

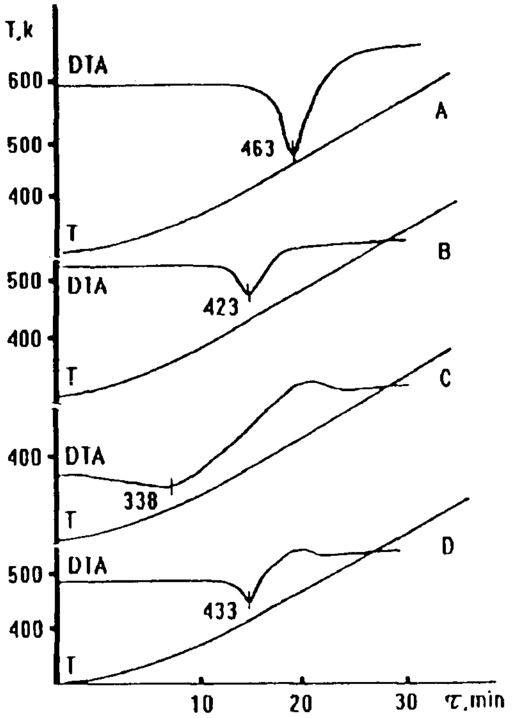

Fig. 3. DTA curves of (A) $Cu(OH)_2$, and samples prepared by (B) 10 min of dry grinding, (C) 1 h of dry grinding and (D) 1 h of wet grinding.

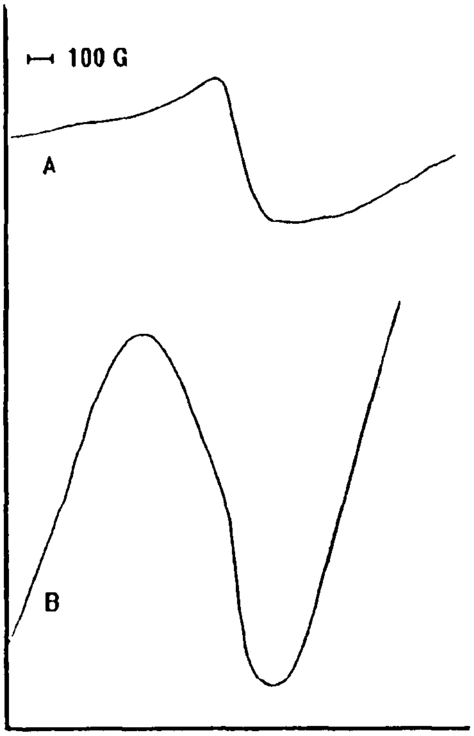

Fig. 4. ESR spectra of (A) $Cu(OH)_2$ and (B) sample obtained after 1 h of dry grinding.

after a prolonged treatment (1 h), when E_M is visible at 433 K (Fig. 3, curve D). A comparison of these data from the thermal analysis of the samples obtained by methods A and B leads to the conclusion that, in the case of dry grinding, the activation of $Cu(OH)_2$ is more pronounced than is the activation after wet grinding.

The DTA curves of the samples after 1 h of mechanical treatment by both methods reveal additional exothermic effects (Fig. 3, curves C and D). The presence of these effects is a result of the defect structure of the mechanically treated samples. Energy is accumulated in the defective regions [1, 10] and is then liberated with increasing temperature, forming an exothermic peak on the DTA curve.

The specific surface areas of the samples obtained by dry grinding have been measured. The values obtained are as follows: 22 $m^2\ g^{-1}$ for the initial $Cu(OH)_2$ sample; 20 $m^2\ g^{-1}$ for the sample obtained after 10 min of grinding; 20 $m^2\ g^{-1}$ after 30 min of grinding; 36 $m^2\ g^{-1}$ after 1 h of grinding; 35 $m^2\ g^{-1}$ after 3 h of grinding.

After 1 h of grinding, the specific surface area increases to 36 $m^2\ g^{-1}$. As already mentioned, this sample contains CuO and a small amount of not completely decomposed $Cu(OH)_2$. Hence the increase in specific surface area may be related to the considerable advancement of the mechanochemical decomposition of $Cu(OH)_2$. The same trend has been observed in the

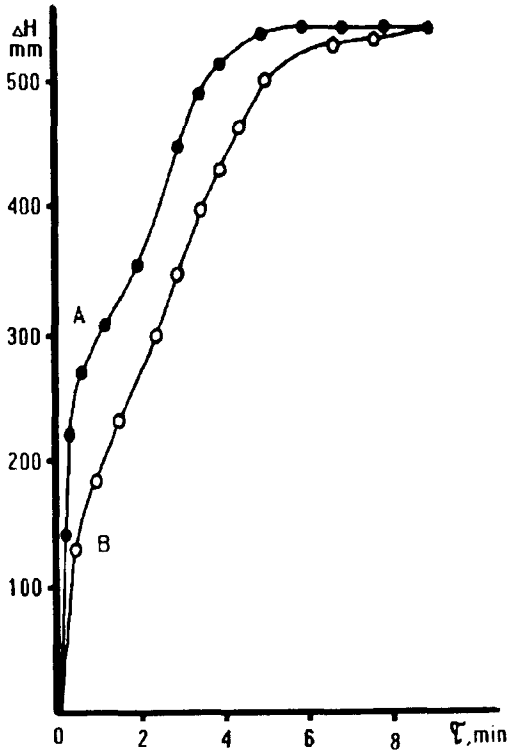

Fig. 5. Change in hydrogen pressure (ΔH) in the calibrated volume of a static circulation apparatus during reduction of CuO. Reduction of CuO obtained (a) by 3 h of dry grinding and (B) by thermal decomposition.

ESR data. Figure 4 presents the ESR spectra of two samples. The initial $Cu(OH)_2$ sample has a line width of about 300 *G*, whereas the linewidth of about 600 *G* corresponds to the sample obtained after 1 h of dry grinding. It is obvious that the line width increases with the progress of mechanochemical dehydration. The changes observed indicate a weakening of the spin–spin interaction between the separate paramagnetic particles.

The reduction of CuO synthesized by 3 h of dry grinding of $Cu(OH)_2$, and the CuO obtained by thermal decomposition of the same $Cu(OH)_2$ during 3 h of isothermal heating at 473 K, has been studied (Fig. 5, curves A and B). The figure shows that the reduction of CuO obtained by method A occurs faster. The specific surface area of CuO synthesized by thermal decomposition ($50\ m^2\ g^{-1}$) is larger than that of CuO obtained by dry grinding ($35\ m^2\ g^{-1}$). Therefore, the more rapid reduction of CuO obtained by method A can be ascribed to its more defect-type structure formed as a result of the mechanochemical decomposition and mechanical activation.

4. Conclusions

The results obtained permit the assertion that the system $Cu(OH)_2$–CuO is appropriate for investigation from a mechanochemical view point. In addition to the mechanochemical decomposition of $Cu(OH)_2$, the activation of the initial $Cu(OH)_2$ sample and of the CuO formed as a final product take place.

Several effects resulting from mechanochemical activation – such as broadening of the X-ray diffractional lines, the presence of additional exothermic peaks, a decrease in the temperature of thermal decomposition of the mechanically treated $Cu(OH)_2$, and the quicker reduction of the CuO obtained mechanochemically – have shown that mechanically treated samples have a defect structure.

In this paper, it has been shown that dry grinding is more efficient than wet (cyclohexane) grinding and leads to quicker decomposition of $Cu(OH)_2$.

References

1 J.L. Rendon, J. Cornejo and P. Arambari, *J. Coloid Inter. Sci., 34* (1983) 546.
2 E. Mendelovici, R. Vilalba and A. Sagarzazu, *Mater. Res. Bull., 17* (1982) 244.
3 R. Gomes-Villacieras, J. Morales and J. Tirado, *J. Chem. Soc., Chem. Commun., (8)* (1984) 559.
4 J. Morales and J. Tirado, *J. Mater. Sci. Lett., 5* (1986) 1295.
5 E. Barrios, L. Herman and J. Morales, *J. Colloid Inter. Sci., 113* (1986) 212.
6 D.G. Klissurski, V.N. Blaskov, J. Subrt and K. Bechine, *Collect. Czech. Chem. Commun., 51* (1986) 2737.
7 R. Gomes-Villacieras, L. Herman, J. Morales and J. Tirado, *Mater. Res. Bull., 22* (1987) 513.
8 G. Bliznakov, U. Bakarjiev and E. Gotcheva, *Commun. Dept. Chem., Bulgarian Academy of Sciences, IV* (1) (1971) 11.
9 L.A. Isupova, V.Yu. Alejsandrov, V.V. Popovskii, V.A. Blashov, A.A. Davydov, A.A. Budneva and N.N. Kryukova, *React. Kinet. Catal. Lett., 31* (1985) 195.
10 H. Imai and M. Senna, *J. Appl. Phys., 49* (1978) 4433.