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Aspects of the synthesis of copper hydride and supported copper hydride

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The synthesis of copper hydride powder is described. The material is characterised by powder X-ray diffraction and transmission electron microscopy. The hydride was precipitated in the presence of, or mechanically mixed with, catalytically interesting supports (alumina, silica, ceria and zinc oxide) provided all operations are carried out under inert atmospheres. The supported hydride may be thermally decomposed at low temperatures to yield suitably sized copper particles directly on the support. This novel route is likely to lead to catalytically active materials. It is found that copper hydride is stable on non-basic supports but decomposes on contact with strongly basic surfaces.

Keywords: Copper hydride; copper; silica; alumina; ceria; zinc oxide; decomposition; fine particles; electron microscopy; supported metals

1. Introduction

Copper hydride, CuH, is unique among the binary metal hydrides in that it is the only hydride synthesized in aqueous media [1,2]. Its properties have been extensively reported including its crystal structure [3,4]. It is thermally unstable at room temperature – and is normally stored at −5°C [5,6]. In addition, CuH readily decomposes in the beam of a transmission electron microscope, yielding dispersed nanometer-sized copper particles [7,8]. This ease of decomposition has been exploited by Kurata et al. [9] who patented a route to the production of highly activated copper catalysts by the thermal decomposition of copper hydride at temperatures below 100°C.

This paper describes the optimum conditions for the synthesis of copper hydride both in an unsupported form and also in contact with catalytically interesting acidic and basic supports, i.e. silica, ceria, alumina and zinc oxide. We note that the low temperature thermal decomposition route to the synthesis of copper from the hydride is in contrast to the standard methods of production of dispersed metal catalysts which generally involve drying and calcination stages (utilizing temperatures as high as 300–500°C) followed by hydrogen reduction [10] and ought, therefore, to offer an interesting and alternative route to catalyst synthesis. In addition we emphasise that the decomposition of CuH should result in the generation of metallic copper in the absence of any charge-balancing anions since in this case such anions are released from the surface (as hydrogen gas).

Both powder X-ray diffraction and transmission electron microscopy have been used to determine the optimum conditions for the synthesis of the hydride and the decomposition process.

2. Experimental

2.1. CHARACTERISATION

Powder X-ray diffraction data (PXRD) were recorded using Cu K_α radiation on a Phillips PW 1050 diffractometer, with a PW 1710 control unit interfaced to a BBC micro-computer system. A JEOL 200CX TEMSCAN electron microscope was used for low magnification work. High resolution images were obtained using a modified JEOL 200CX microscope [11]. For transmission electron microscopy (TEM) a small quantity of sample material was dispersed in dry diethyl ether and deposited onto a holey carbon support grid.

2.2. SYNTHESIS

The preparation of the hydride followed closely that given in the literature [1,2] and involved the reaction of aqueous copper sulphate with hypophosphorous acid in the presence of sulphuric acid:

$$4Cu^{2+} + 6H_2PO_2^- + 6H_2O \xrightarrow{H^+} 4CuH_{(ppt)} + 6H_2PO_3^- + 8H^+.$$

Optimum pH conditions (close to 1) resulted from the mixing of a solution of 100 ml 0.1 M $CuSO_4 \cdot 5H_2O$ (minimum 99.5% AnalaR, BDH Chemicals) with 20 ml 0.75 M H_2SO_4 ($\approx 98\%$, Fisons) which was added dropwise over a 15 min period to 280 ml 0.32 M hypophosphorous acid (50 wt% in water, Aldrich Chemical Co.) maintained at 55°C. All procedures were done under an inert atmosphere (N_2 or Ar) using deaerated solutions (N_2 purged).

The resulting finely divided red-brown precipitate was cooled in ice, filtered, washed with absolute alcohol and diethyl ether and partially dried in an inert atmosphere. The solid product retained approximately 40% by weight of solvent – it was found that when more extensively dried the copper hydride sponta-

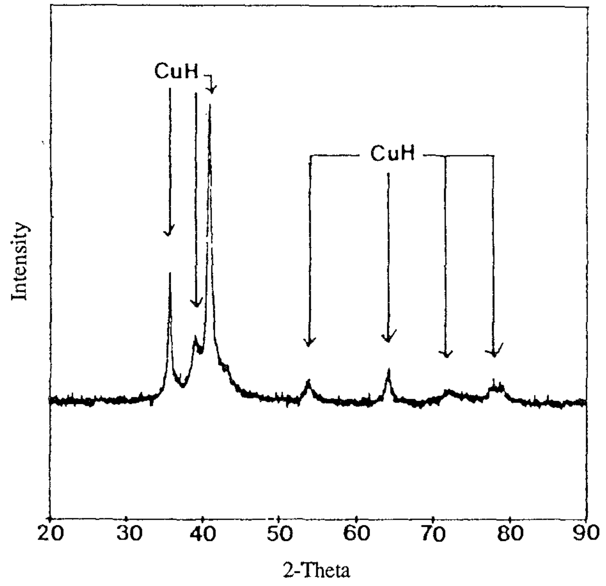

Fig. 1. Room temperature PXRD pattern of the product obtained for CuH synthesised under an atmosphere of nitrogen. CuH positions are based on values given in the JCPDS file 8-256.

neously decomposed exothermically at ambient temperature – and was stored at 0°C.

Two silica supports (Aerosil 200, Degussa; Kieselgel 60-9385, Merck) as well as γ-alumina (Sol-gel material), ceria (Reacton, 99.9%) and zinc oxide (Fisons AR, 99.5%) were chosen as initial catalyst supports to provide a range of surface acidities and basicities. Samples were prepared either by precipitation of the hydride in the presence of the support or by mechanically mixing the separately prepared hydride with the support using dry diethyl ether as the dispersion medium.

3. Results and discussion

Fig. 1 illustrates the powder XRD pattern obtained for pure CuH. Standard 2θ (powder pattern) values for the hydride [12] are compared to those obtained by us in table 1.

An electron micrograph of copper hydride is shown in fig. 2. At low magnification and at low illumination, the hydride can be seen as fairly thick agglomerates. With more intense electron irradiation the hydride appears to melt and decomposes to disperse fine particles of copper over the holey carbon support [13], see fig. 3. Some of these particles are highly defective with dimensions in the nanometre size domain [7]. We will report elsewhere on the defect nature of

Table 1
XRD data. Cu K_α radiation $\lambda = 1.54$

$2\theta_{calc}$ (deg)	$2\theta_{obs}$ (deg)	d_{calc} (Å)	d_{obs} (Å)
35.45	35.52	2.53	2.52
38.96	39.03	2.31	2.31
40.61	40.65	2.22	2.22
53.55	53.50	1.71	1.71
63.69	63.86	1.46	1.46
71.72	71.75	1.32	1.31
77.25	77.40	1.23	1.23

the crystallites. Attempts are made in this study to thermally decompose the hydride in contact with the supports to generate dispersed metallic particles on the support surface.

3.1. CuH ON SILICA

Heating to 95°C in argon of the supported hydride (prepared by mechanical mixing) resulted in the production of pure copper metal (in the absence of any

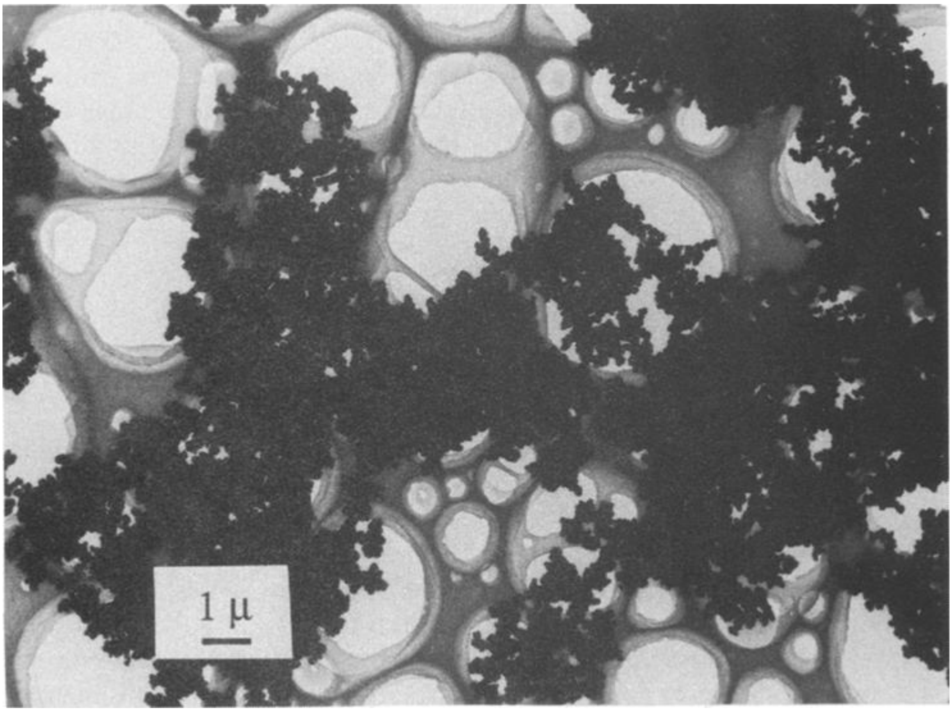

Fig. 2. Low magnification electron micrograph of CuH with minimal beam exposure and damage.

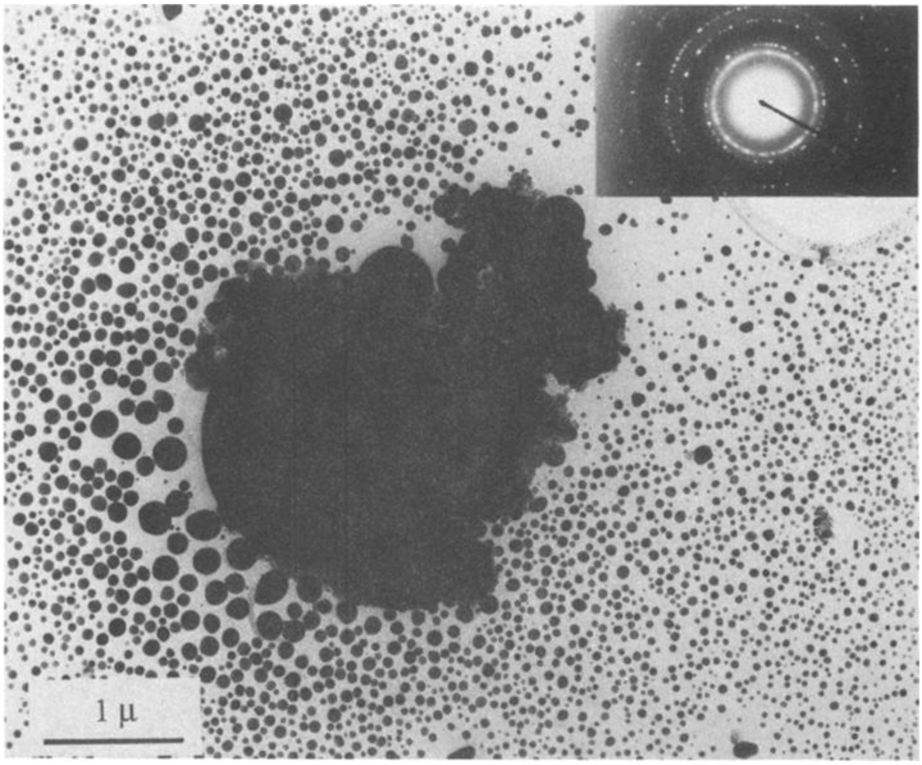

Fig. 3. Residue for CuH after beam damage. The larger masses are residual metal. The small particles which range in size from several microns down to nanometres are deposited metallic copper. The insert shows the electron diffraction pattern from a cluster of these particles with the polycrystalline pattern indexing as copper metal.

detectable oxide) on Aerosil 200, see fig. 4. Atomic absorption analysis (AA) showed for this sample that the total copper content was approximately 10% by weight. The successful preparation of both the supported hydride and its decomposition to the supported metal requires an inert atmosphere.

Carrying out the synthesis using the precipitation method with Kieselgel 60 was less successful, in that copper and, to a much lesser extent, copper(I) oxide impurities were also produced. The reason for these impurities is thought not to be due to direct interaction of the hydride with the slightly acidic [14] SiO_2 support, but rather with the relatively large amount of water available on the very large surface area, porous Kieselgel 60 [6]. The fact that copper hydride is stable in contact with the non-porous Aerosil 200 supports this view. AA analysis of the decomposed sample showed the total copper content to be approximately 20 wt%. Subsequent heating in 5% H_2/N_2 at 240°C resulted in the production of pure copper on the Kieselgel.

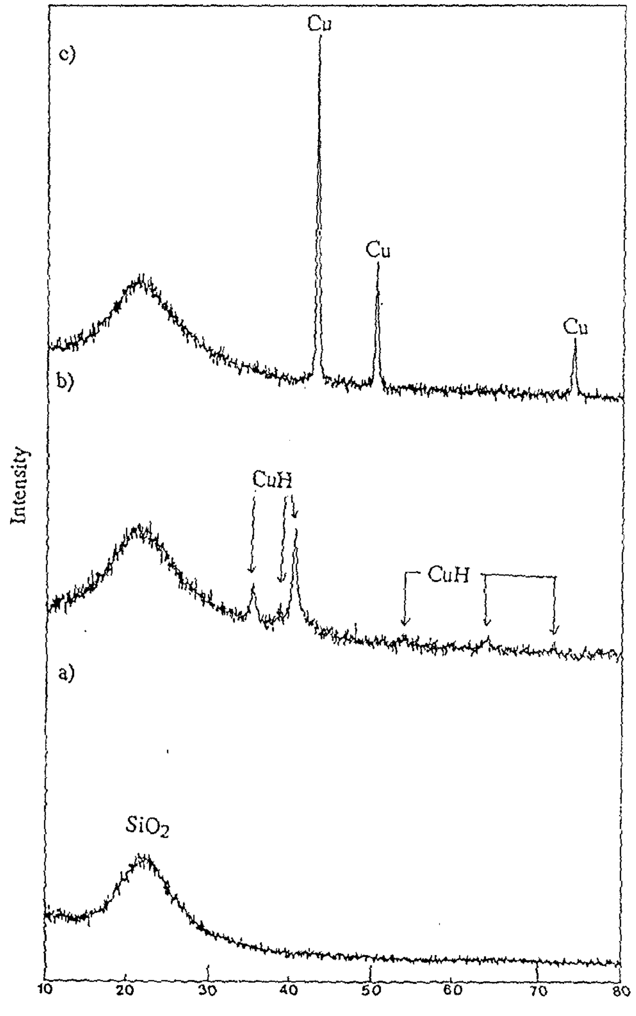

Fig. 4. (a) Pure Aerosil 200, (b) ≈ 10% CuH on SiO_2, (c) ≈ 10% Cu on SiO_2.

3.2. CuH ON CERIA

The XRD pattern for a sample obtained of an ≈ 50% copper hydride on cerium oxide by the precipitation method can be seen in fig. 5a. No impurity peaks (copper oxide) are visible although, as will be seen below in the case of zinc oxide, the support particles are relatively large and small amounts of oxide impurity present would not be easily identifiable against the intense cerium oxide peaks. (Decomposition of the supported hydride sample in air at 110°C produced small particles of copper(I) oxide.)

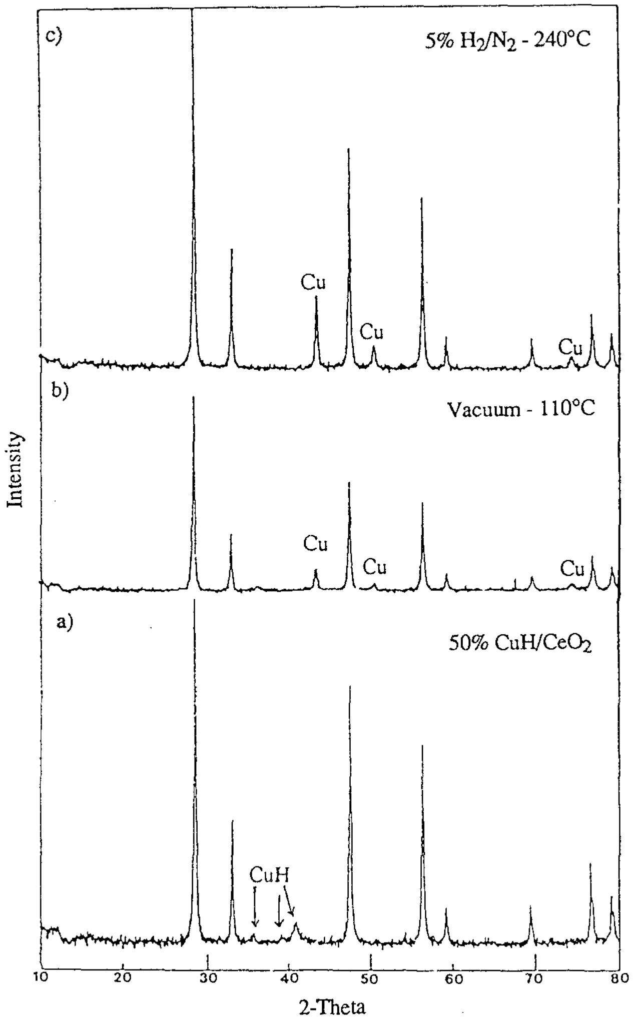

Fig. 5. (a) ≈ 50% CuH on CeO_2, (b) ≈ 50% CuH on CeO_2 after decomposition under vacuum (110°C), (c) ≈ 50% CuH on CeO_2 after decomposition in 5% H_2 in N_2 (240°C).

Figs. 5b and 5c clearly illustrate that decomposition of the hydride on cerium oxide, both under vacuum and in 5% hydrogen in nitrogen, produces the supported copper metal. AA analysis gave the copper content for these two samples as being close to 21% by weight. It is interesting to note that the intensity of the copper peak after decomposition at 110°C under vacuum (16 h) is considerably lower than that obtained from decomposition in 5% hydrogen in nitrogen at 240°C (3 h). Taking into consideration the time spent at each temperature and the AA results, the most likely explanation for this is that the copper particles formed at 110°C are smaller. Slow sintering of the copper particles may have occurred at 240°C, giving larger particles of more uniform size.

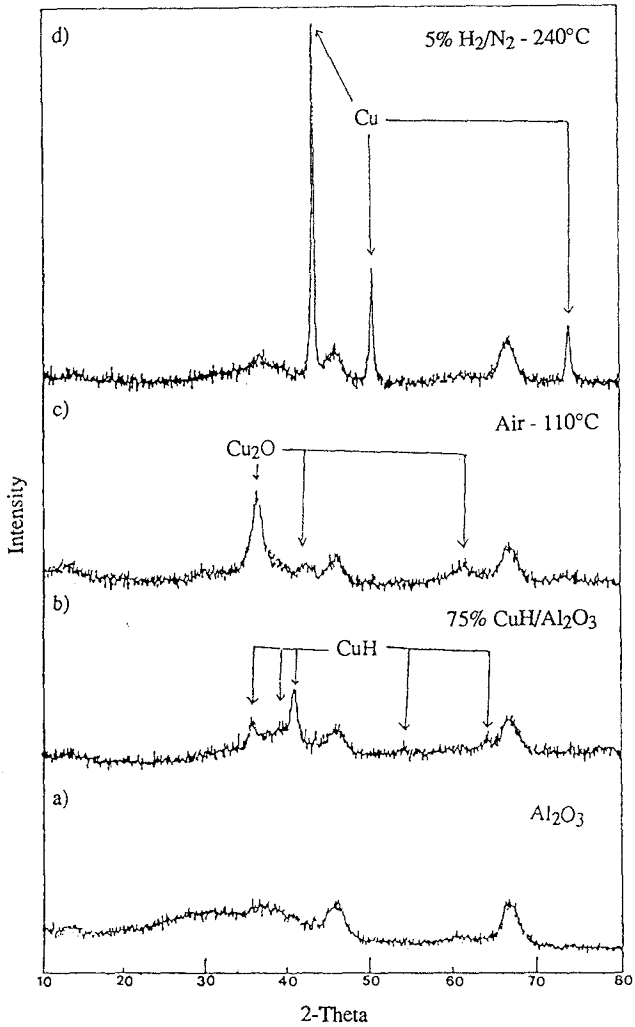

Fig. 6. (a) Pure Al_2O_3, (b) ≈ 75% CuH/Al_2O_3, (c) after exposure of (b) to air for 24 h and (d) after reduction in 5% H_2/N_2.

3.3. CuH ON ALUMINA

Figs. 6a and 6b clearly show that fine particles of copper hydride on alumina may be obtained using the precipitation procedure. Heating the supported hydride in air at 110°C for 3 h resulted in the production of very small particles of copper(I) oxide with no clear evidence of copper metal formation see fig. 6c. As in the case of the ceria-supported hydride heat treatment of the sample in a 5% H_2/N_2 mixture at 240°C produces pure copper metal, see fig. 6d. AA analysis gave the total copper content to be close 20% by weight. The copper

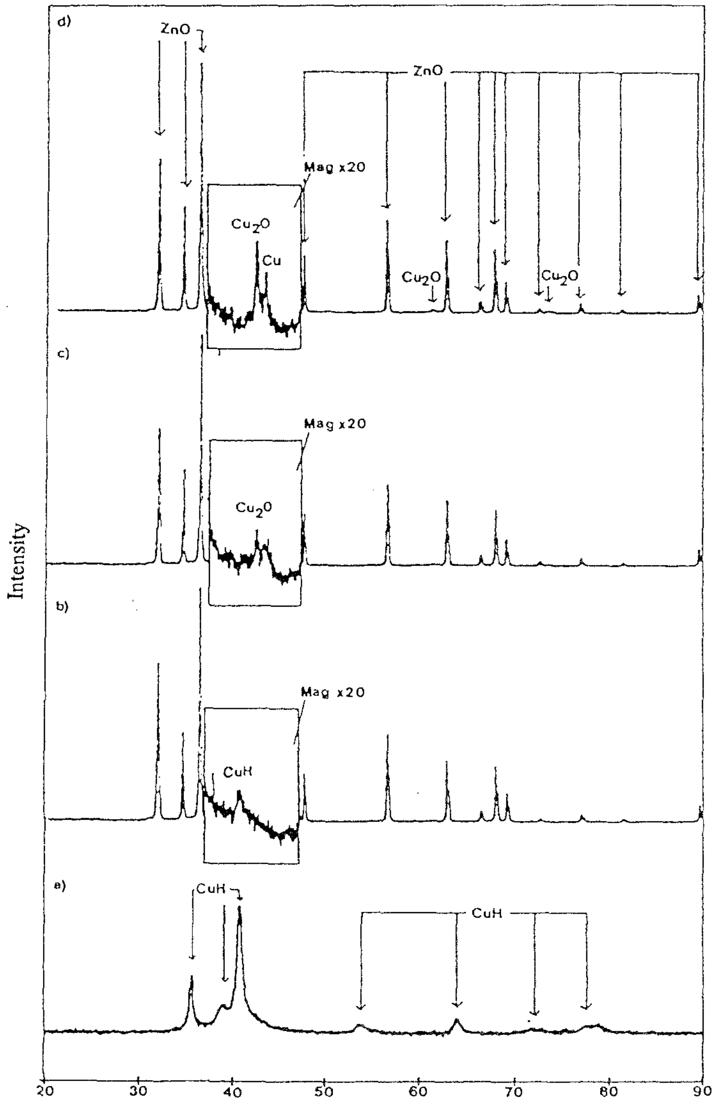

Fig. 7. (a) CuH, (b) fresh sample of ≈ 10% CuH on ZnO, (c) ≈ 10% CuH on ZnO, 24 h after preparation, and (d) sample (b) after heating at 95°C for 3 h under argon, producing Cu on ZnO.

peaks are much sharper and more intense than those due to copper(I) oxide again suggesting possible sintering of the copper particles.

3.4. CuH ON ZINC OXIDE

The mechanical mixing technique, using 10 wt% CuH was successful, figs. 7a and 7b. XRD analysis carried out on the same sample stored in air for 24 h after the initial preparation indicated that the copper hydride had decomposed to copper(I) oxide and small amounts of copper, see fig. 7c. This suggests that the hydride, when placed in contact with zinc oxide, is unstable, presumably due to its strongly basic properties [14].

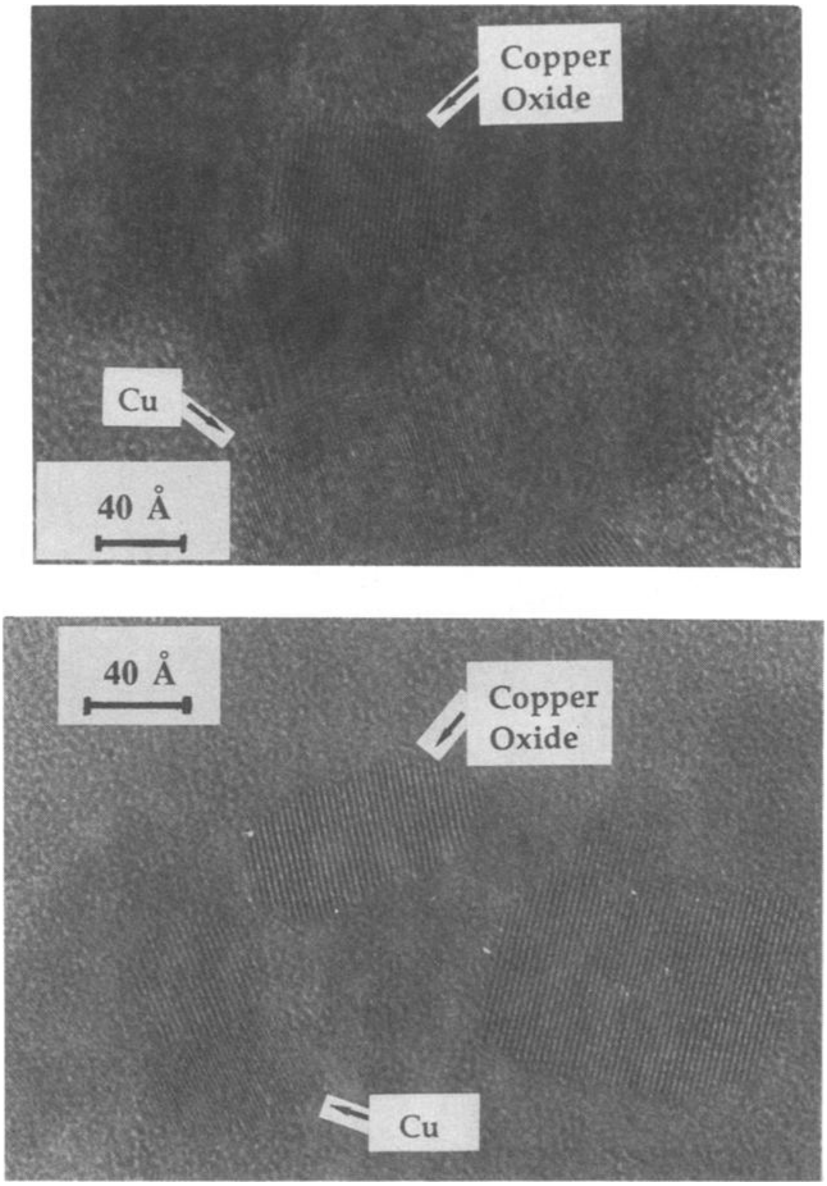

Fig. 8. Micrographs of a sample of copper oxide on a zinc oxide support. comparison of the fringe spacing exhibited by the particles suggests that the wider spacings correspond to copper oxide and the narrower ones to copper.

Preparation of a 10% loading of copper hydride in the presence of the support via the precipitation method proved to be impossible. During the course of the preparation, the temperature of the reaction mixture increased rapidly resulting in the formation of a pale blue "cement" (a zinc oxide and copper sulphate mixture). No copper hydride precipitate was produced – the reactant mixture having too high a pH for CuH formation. Therefore, for zinc oxide as a support the only viable route to supported copper metal is via thermal decomposition of the mechanically mixed hydride, see fig. 7d.

Micrographs obtained for the mechanically mixed copper hydride on zinc oxide (see fig. 8) show the presence of 40–50 Å diameter particles with two different sets of fringe spacings. It is thought that beam induced decomposition of the hydride is occurring to produce copper particles and that an earlier process resulted in the copper oxide particles; from the PXRD results suggest that the oxide particles were present in the sample prior to examination in the microscope.

4. Concluding remarks

Powder X-ray diffraction is a suitable fingerprinting technique for the identification and characterisation of copper hydride and, using this technique, a reproducible preparation procedure for copper hydride has been established. It is shown that suitably sized copper particles on silica, ceria, alumina and zinc oxide supports may be obtained via the low-temperature thermal decomposition of the hydride provided all operations are carried out under an inert atmosphere. It is not possible, however, to isolate zinc oxide supported copper hydride due to the instability of the hydride in the presence of strongly basic materials. Copper hydride, however, may be readily supported on an acidic support such as silica.

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