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IN-SITU STUDY OF REDUCTION OF COPPER CATALYSTS

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Isothermal hydrogen interaction with unsupported CuO and 15%CuO/ZnO at about 419–427 K has been followed by in-situ X-ray diffraction as monoclinic CuO is replaced by zero-valent Cu^0 without direct evidence of formation of intermediate Cu_2O. Surprisingly, less than half of the copper phases within such samples is X-ray detectable. X-ray analysis indicates that reduction of crystalline CuO in CuO/ZnO catalysts may not be retarded by ZnO, but TPR-TGA suggests that reduction of more amorphous CuO may be so retarded.

1. Introduction

Copper is traditionally used in catalysis of methanol synthesis in the supported state (e.g. $Cu/ZnO/Al_2O_3$ or $Cu/ZnO/Cr_2O_3$ [1]). However, there is great uncertainty and current interest in the chemical state of this copper under reaction conditions. Indeed, disagreement about its oxidation state exists [2], with some groups emphasising the importance of a zero-valent component [3] and others stressing the role of the component in a positive oxidation-state [4]; doubtless a mixture of copper oxidation states exist within such catalysts during reactions of $CO/CO_2/H_2$ mixtures and is indeed probably changed by the reactants themselves. CuO and CuO/ZnO then are model samples for methanol synthesis catalysts [5] and have been studied here using in-situ X-ray diffraction in terms of the phases present in a hydrogen atmosphere at relevant temperatures.

2. Catalysts

Unsupported CuO and 15%CuO/ZnO were prepared by co-precipitation of aqueous solutions of cupric nitrate (Johnson Matthey; Puratronic) with and without zinc acetate (AnalaR) with NH_4HCO_3 or $(NH_4)_2CO_3$. For CuO the precipitate was washed, dried (383 K, 24 h) and calcined (600 K; 1.5 h), while the 15%CuO/ZnO was prepared from the washed precipitate by drying (393 K, 16 h) and calcination (473 K, 16 h). No significant impurities were found in CuO or CuO/ZnO samples used here.

3. Characterisation methods

Scanning electron microscopy and X-ray photoelectron spectroscopy (Kratos ES300 spectrometer with Al incident radiation at 1468.6 eV) were used to characterise samples before and after reduction. Total surface areas were estimated by BET analysis of N_2 physical adsorption at 78 K (Carlo Erba 1800 and 1826 instruments) after outgassing for 16 h. The active Cu^0 surface area in reduced Cu/ZnO was determined volumetrically by N_2O decomposition [6] at ambient temperature (with N_2O removal at 78 K) and oxygen chemisorption at 78 K and 5.3 kPa. In both cases an adsorption stoichiometry Cu : O of 2 was assumed and it was judged that there were 1.41×10^{19} Cu atoms per m^2. The reducibility of samples was determined in a temperature-programmed manner using gravimmetry for CuO and also determination of H_2 consumption (TPR) for 15%CuO/ZnO. The isothermal rate and extent of hydrogen sorption by CuO sample at 398 K were determined volumetrically in a system described previously [7]. An in-situ X-ray cell [8] was used to follow the isothermal reduction of CuO and 15%CuO/ZnO when this was held in a vertical diffractometer (Philips

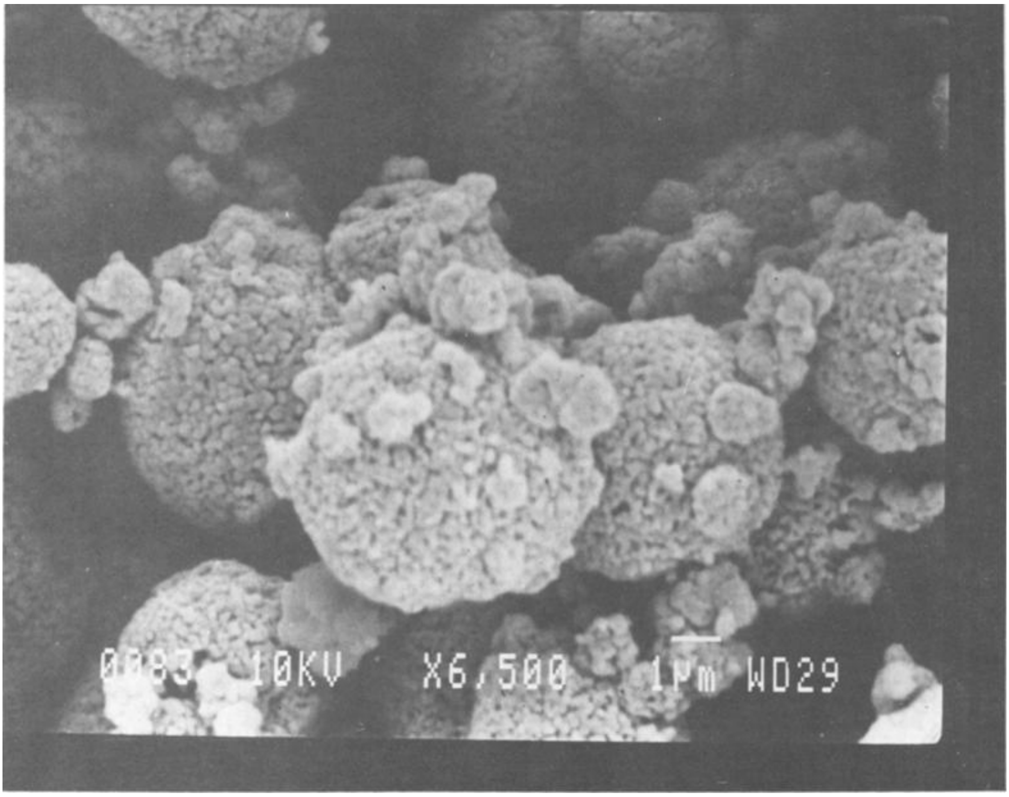

Fig. 1. Scanning electron micrographs of unsupported CuO before (a) and after (b) interaction with hydrogen at 398 K to the point in fig. 2 where the sorption of hydrogen was complete.

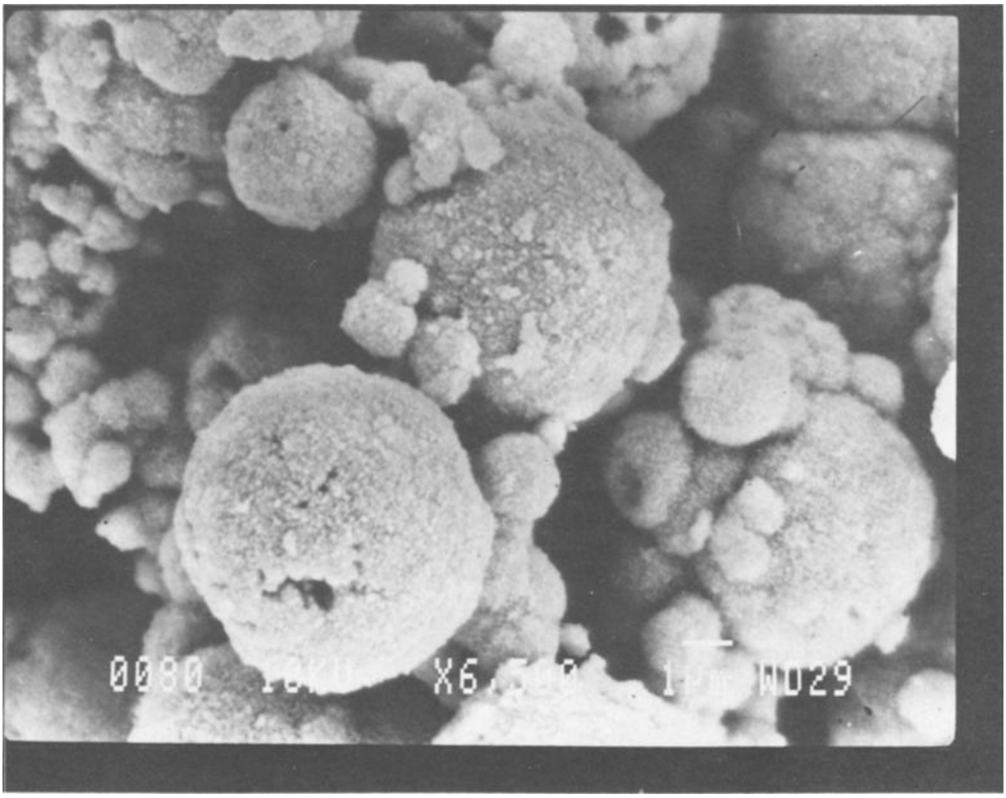

Fig. 1 (continued).

PW1710) operating with Ni-filtered CuK_α radiation (average wavelength 0.15418 nm) at 40 kV and 30 mA with N_2 or H_2 flowing at 101 kPa.

4. Characterisation results

The total surface areas of CuO and 15%CuO/ZnO were found to be 30 $m^2 \cdot g^{-1}$ and 18.6 $m^2 \cdot g^{-1}$ respectively. X-ray photoelectron spectroscopic shake-up satellites suggested both CuO and 15%CuO/ZnO samples contained divalent copper. Tga and temperature-programmed reduction confirmed almost total reduction of divalent copper was observed in both samples. Interestingly, tga and tpr suggested that CuO and 15%CuO reduced in 101 kPa H_2 at a maximum rate at 430 K and 473 K respectively; in other words ZnO decreased the rate of CuO reduction as predicted [9]. It was therefore judged that isothermal in-situ reduction studies should be carried out below 430 K and might then reveal mechanisms, kinetics and intermediates in CuO reduction in these samples with analysis as a function of time. Even at 360 K CuO is known to reduce [10] albeit slowly.

Scanning electron microscopy (see fig. 1) showed that on treatment with hydrogen at 101 kPa at 398 K there were no major morphological changes of CuO aggregates, although the primary particle size did increase on reduction. Hence the temperatures chosen here for isothermal in-situ studies of this exothermic reduction of these catalysts were appropriate and substantially avoided sintering.

5. Results of hydrogen sorption-reduction

Figure 2 shows duplicate isotherms for hydrogen uptake by unsupported CuO at 398 K; it is clear that H_2 uptake is approaching completion at close to 3 kPa at this temperature; presumably a maximum value corresponding to complete reduction would eventually have been reached at a slightly higher pressure. Obviously, the isotherms provide no direct evidence that Cu^0 (or Cu_2O) is actually formed in preference to intermediate hydroxides (e.g. CuO certainly adsorbs and absorbs hydrogen [11]). Figure 3 shows hydrogen is taken up by the CuO at 398 K and 101 kPa at a constant rate over the whole time of measurement; since these kinetic measurements are in static hydrogen it is not surprising that they are slower than in XRD analysis in flowing hydrogen (see Figure 4) or vacuum methods (see Figure 2) where product water is continuously removed.

6. Results of in-situ X-ray analysis

Figures 4 and 5 show in-situ X-ray analysis as a function of time in flowing H_2 (101 kPa) at 419 K ± 1 K (CuO) or 427 K ± 2 K (CuO/ZnO). The (111) peak of monoclinic CuO (38.71° 2O; $d = 0.2527$ nm) present in both samples initially decreases in intensity with reduction time, while simultaneously the (111) peak of Cu(43.24° 2O; $d = 0.2090$ nm) increases in intensity (from a nil concentration in CuO, but from a small but finite value in 15%CuO/ZnO). Only limited in-situ X-ray analysis of this reduction has been attempted previously [12]. Samples were separately treated at 573 K in flowing hydrogen until completely reduced; these were mixed in known amounts with the unreduced catalysts. Using these mixtures as calibrants it was possible to calculate the percentage of CuO reduced and the percentage of Cu produced from the data in these figures. Such results are shown as S-shaped reduction profiles in the same figures. These have been generally seen for CuO reduction [13] and have been attributed to autocatalysis of the reduction process. Although the % CuO reduced approximately equals the % Cu produced (and so there is a good mass-balance between reactant CuO and product Cu in the X-ray detectable phases), neither correspond to the entire copper content of these materials. Interestingly, in these relatively well-crystallised material there is no detectable intermediate phase between CuO and Cu. However, the majority of the copper appears to be in a state which cannot be probed by the X-ray

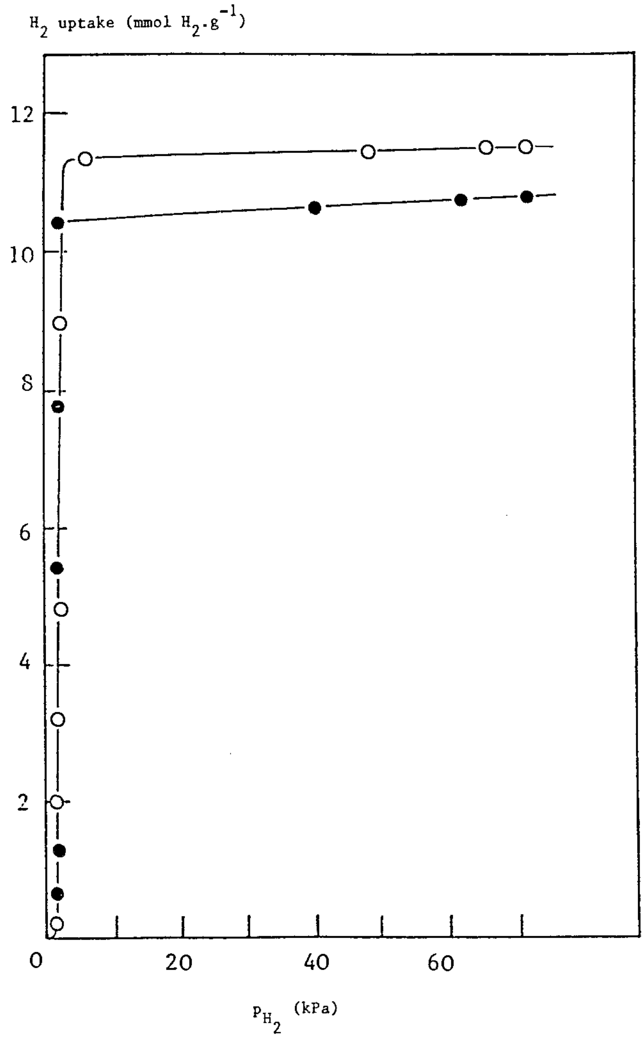

Fig. 2. Hydrogen sorption isotherms for CuO at 398 K. Open and black symbols denote duplicate runs.

approach here. X-ray diffraction line broadening (XRDLB) estimated the average crystallite size of X-ray detectable CuO and Cu phases in 15%CuO/ZnO to be 89.7 nm and 116.1 nm respectively, assuming a Scherrer constant of 0.9. These correspond to surface areas of 7.50 $m^2 \cdot gCu^{-1}$ and 6.95 $m^2 \cdot gCu^{-1}$ respectively. For the same reduced sample N_2O decomposition and O_2 chemisorption suggested Cu surface areas of 9.1 and 8.5 $m^2 \cdot gCu^{-1}$; since these are close to those estimated by XRDLB it seems likely that the non-X-ray detectable material is amorphous and of low-order, rather than merely finely dispersed (when it would have raised chemisorption areas but not XRDLB ones). It should however be remembered that N_2O also decomposes on copper oxides [6] and this means that such N_2O data are not themselves unequivocal.

7. Discussion

The Avrami relationship for the kinetics of a nucleation-growth transition

$$\exp(-kt^n) = (1 - x)$$

relates the volume fraction of the transformed phase x to time t. Here x was calculated in two ways (i) from the percentage of Cu formed in X-ray diffraction measurements and also (ii) the number of moles of hydrogen consumed in volumetric measurements (assuming this was equal to the number of moles of Cu formed). The X-ray data do generally obey the relationship at longer times with

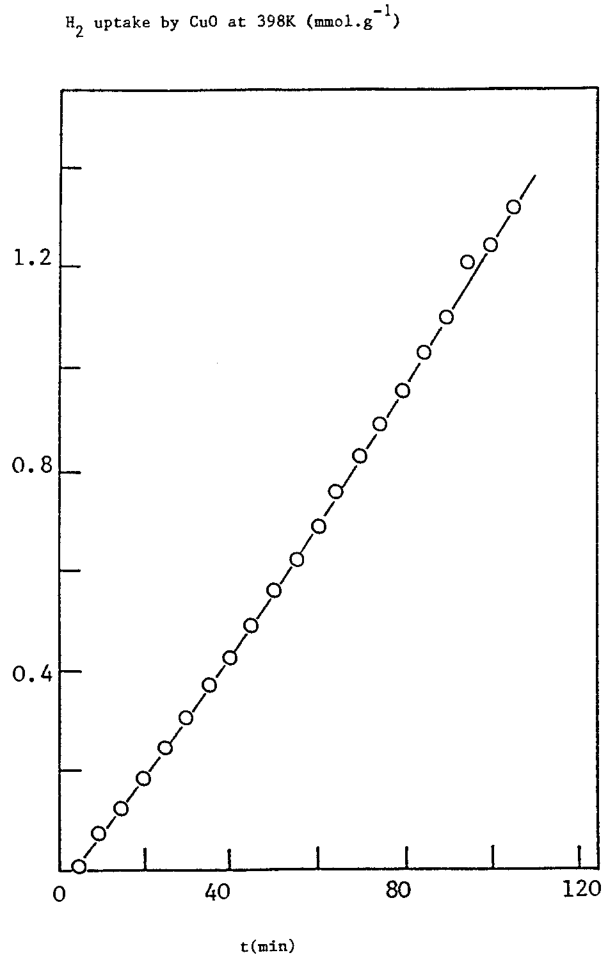

Fig. 3. Rate of hydrogen sorption by unsupported CuO at 398 K and 101 kPa H_2.

different values of integer n for the two samples (i.e. 1.65 for CuO reduction and 4.27 for 15%CuO/ZnO reduction). However, the volumetrically-derived data certainly does not obey the relationship, and since the rate of hydrogen consumption by CuO was almost constant with time (see fig. 3) this is not surprising.

Previous studies [14] of silica-supported Pt have found that as little as 30% of the metal may be in a form which is X-ray detectable, although this increases on heating at 373–773 K. Similarly, the present work suggests that much of the copper in such catalysts is in a low-order or amorphous state. This is consistent with other earlier work. Thus Klier and co-workers [15] have concluded that Cu/ZnO contains both metal microcrystallites and amorphous Cu^+ in the ZnO lattice (although this must be contrasted with other reports [16] that less than 2% of copper in such catalysts is not zero-valent). Nevertheless, much copper in such catalysts cannot be entirely resolved by electron microscopy [17]. Since zero-valent copper surface areas may define activity of supported catalysts in CO/CO_2 hydrogenation to methanol [3], present in-situ X-ray analysis of catalyst reduction are clearly relevant and complimentary to previous XPS and IR analyses [5,18]. Nevertheless, they will need to be augmented by an EXAFS structural probe,

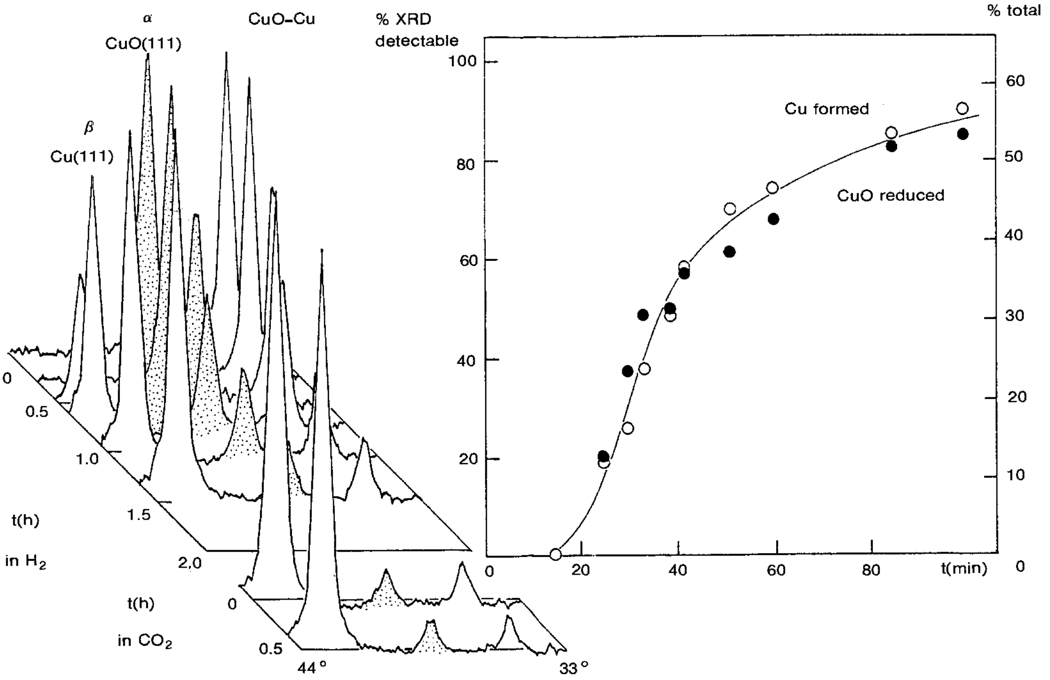

Fig. 4. X-ray diffraction patterns of CuO as a function of time in flowing H_2 (30 cm^3 min^{-1}; 101 kPa) at 419 K and 427 K respectively. Attention was given to the intensity of the shaded α-peak of CuO(111) and the β-peak of Cu^0(111). Also shown is the subsequent interaction of the reduced catalysts with CO_2 (30 cm^3 min^{-1} 101 kPa) at the same temperature. Percentages of CuO reduced and Cu formed during reduction under these conditions are plotted as the percentage of X-ray detectable material and also as the percentage of the total copper content of the catalysts as a function of time.

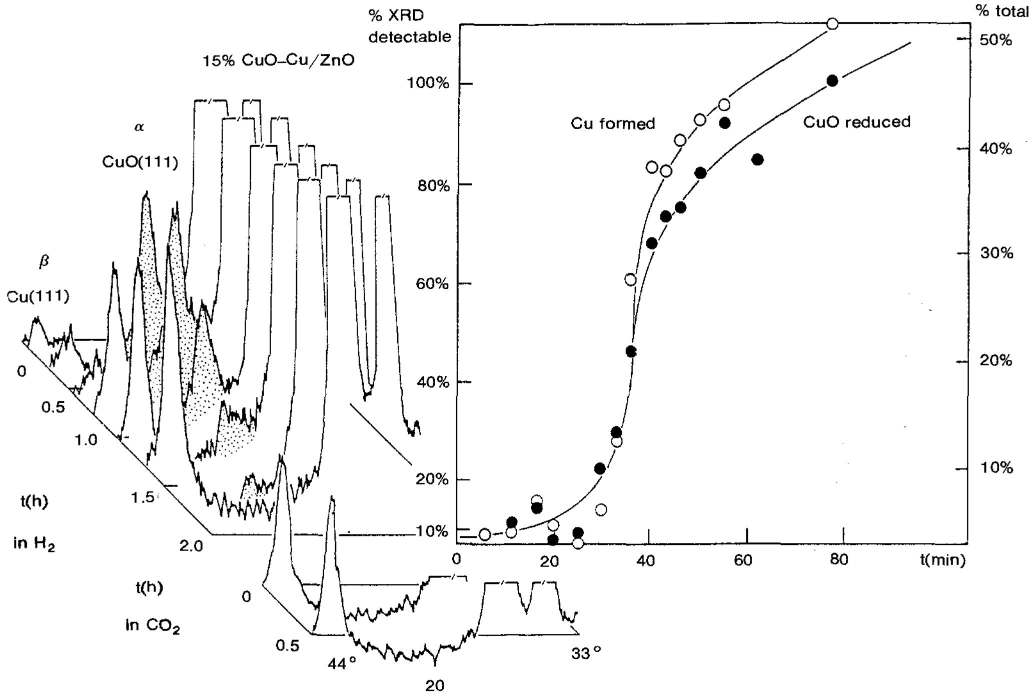

Fig. 5. Analysis of 15%CuO/ZnO as for CuO in Figure 4 except that this was at 427 K.

especially with regard to the critical low-order copper phases. It is quite possible that further in-situ studies of these reductions will reveal meta-stable intermediates (just as they appear during Cu oxidation [19]).

Figures 4 and 5 also show in-situ X-ray diffraction patterns produced when CO_2 at 101 kPa interacts with the prereduced catalysts. It is clear that the fraction of CuO (or Cu_2O) phases is not increased by CO_2. This is not surprising since the equilibrium constant for

$$CO_2 + Cu = CO + CuO$$

at 273 K is only 10^{-15} [20] and bulk oxidation is not therefore expected [21], although it may increase the fractional coverage of oxygen on the Cu surface [22] by adsorption of CO_2, but even this is said to have low probability on Cu(111). Present catalysts have quite high copper dispersions and yet oxidation by CO_2 is still not seen by XRD, although this does probe the less well dispersed Cu.

8. Conclusions

In-situ XRD [23] has been informative concerning the solid crystalline phases present in Cu heterogeneous catalysts under reaction conditions; thus comparison of figs. 4 and 5 suggests that ZnO does not retard the ease of reduction of CuO to

Cu^0 by H_2 under present conditions, in the sense that induction periods and subsequent reduction profiles are very similar for CuO and CuO/ZnO. Further work on the analysis of catalysts during re-oxidation but for the moment CO_2 does not appear to be very effective in re-oxidising metallic copper produced from CuO or CuO/ZnO. There is no direct evidence here of the precise nature of the X-ray amorphous component of the present Cu catalysts. In this particular case EXAFS-XRD work is certainly required to elucidate the state and chemical environment of copper in these important idealised (and subsequently commercial) heterogeneous catalysts. It should be interesting to know how the fraction (and nature) of the low-order phase changed with Cu loading on ZnO and also with the addition of alumina or chromia. Here then XRD and volumetric H_2 uptakes do not indicate the same reduction profiles for CuO to Cu^0 in CuO and CuO/ZnO. XRD suggests that ZnO does not retard the reduction of the X-ray discernable CuO by H_2, but previously [9] thermal analysis has been used to suggest that it does. This could be reconciled if the more crystalline CuO was not in intimate contact with ZnO and then reduced in much the same way as CuO does alone, but highly dispersed amorphous Cu^{2+} phases in better contact with ZnO had their reduction characteristics modified by the ZnO matrix; only EXAFS analysis of the state of Cu in the amorphous (and possibly catalytically-important) phases in such catalysts during reduction will reveal whether this is so. Nevertheless, XRD cannot be probing only the 'spectator' phases in the catalysts and their reducibility.

The absorption of hydrogen by CuO is probably relevant to the apparent sorption of hydrogen by ZnO in CuO/ZnO catalysts, and conductivity measurements of CuO/ZnO during H_2 sorption could prove interesting in the light of suggestions of interstitial hydrogen in ZnO under synthesis conditions [24].

Previously [25], in-situ XRD has been used to probe ammonia synthesis, methanol synthesis, clay, zeolite and V-P-O catalysts; the present work makes a contribution to this important theme of in-situ catalysts characterisation while these are in use under reaction conditions.

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