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Reaction of CuO with hydrogen studied by using synchrotron-based x-ray diffraction

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Abstract

CuO and Cu₂O powders were reacted by hydrogen to study the reduction mechanism and the ionic states of Cu (Cu²⁺, Cu¹⁺ and Cu⁰). The reduction behaviour and the existence of an intermediate state were investigated by using synchrotron-based high-resolution *in situ* x-ray diffraction (S-XRD) techniques. The results revealed that CuO directly reduces to metallic Cu (Cu²⁺ → Cu⁰), under a normal flow of hydrogen. There was no hint of an intermediate state (Cu¹⁺) during the reduction. In certain conditions, however, an intermediate phase (Cu₂O) appears under either very small flow of hydrogen (<1 cm³ min⁻¹) or very fast temperature ramping (>20 °C min⁻¹), suggesting that the reduction kinetics strongly depends on reduction conditions.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The reduction of metal oxides using hydrogen is a frequently used method to prepare active catalysts and electronic devices [1]. Copper oxide is a benchmark system for reduction studies [2, 3]; it provides a logical pathway from an oxidation of state of 2 to 0 (CuO → Cu₄O₃ → Cu₂O → Cu). This system is also used to understand the electronic structure, which reflects different structures and different oxidation states. Compared to their relative importance in industrial applications, however, little is known on the reduction process at a microscopic level, which requires *in situ* investigations. Previous studies dealing with CuO reduction show discrepancy on the production of an intermediate phase, for example. Several authors [2, 4] observed a Cu₂O phase under certain conditions, while Campbell *et al* [5] showed a direct transformation from Cu²⁺ to Cu⁰ using Auger electron spectroscopy (AES) and x-ray

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photoelectron spectroscopy (XPS). There is no clear explanation why the transient species is not seen in such a case. These discrepancies could be a consequence of the different conditions used in the reduction experiments.

To the best of our knowledge, no systematic studies using *in situ* x-ray diffraction data have been reported on bulk CuO and Cu₂O systems. Therefore, we decided to perform a systematic study on the reaction of H₂ with pure powders using *in situ* time-resolved synchrotron-based XRD. The results from this method represent the 'real' state of the copper phase under reduction conditions at subminute intervals, and this technique has been successfully used to study the reduction of NiO [6]. We obtained very interesting conditions for the production of Cu₂O, which is an intermediate in the synthesis of CuO from metallic Cu but does not appear in all the cases during the reduction of CuO.

2. Experiments

Powders of CuO (monoclinic, $a = 4.68 \text{ \AA}$, $b = 3.42 \text{ \AA}$, $c = 5.13 \text{ \AA}$, $\beta = 99.54^\circ$) and Cu₂O (fcc, $a = 4.217 \text{ \AA}$) were obtained from commercial sources (>99.99% purity). Samples were loaded in an open sapphire capillary having an inner diameter of 0.5 mm. To fix the sample position during the gas flow, quartz wools were added on each side of the powder. One end of the capillary was connected to an inlet of 5% H₂ (99.9999% purity) and 95% He (99.9999% purity) gas mixture, and the other end was connected to a gas flow meter to monitor the gas flow rate at an atmosphere (flow rate $\approx 15 \text{ cm}^3 \text{ min}^{-1}$). A residual gas analyser (RGA) was also attached at the end of the flow meter to examine the products after the reaction. A small resistance heater was designed by winding a kanthal wire around the sapphire capillary which contains the sample. A K-type thermocouple was inserted into the capillary near to the powder to maintain an accurate temperature throughout the measurements. Prior to collecting data from the CuO samples, the coefficient of thermal expansion of Y₂O₃ powder was measured from the same set-up to calibrate the actual sample temperature. The result showed a good agreement with the desired and measured sample temperatures.

The time-resolved synchrotron x-ray diffraction data were collected in the temperature range of 150–300 °C at the beam line X7B ($\lambda = 0.9034 \text{ \AA}$) of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) using an MAR345 area detector. The XRD diffraction data with a high order wavevector Q ($\approx 11.5 \text{ \AA}^{-1}$) were obtained at the beamline 1-ID ($\lambda = 0.1536 \text{ \AA}$) of X-ray Operation and Research in the Advanced Photon Source (APS) at Argonne National Laboratory. An identical set-up system was employed for the experiments. From these data, the occupancies of atoms, accurate lattice constants and fraction of phases appearing during the reaction were determined by a Rietveld analysis [7] using the GSAS (general structure analysis system) program [8].

3. Results and discussions

The CuO system exhibits quite interesting results during the reduction process. First, our TPR results (heating rate $6 \text{ }^\circ\text{C min}^{-1}$) indicate that CuO powder starts to reduce near 280 °C under flowing hydrogen, which is slightly (about 20 °C) lower than the temperature for Cu₂O. Second, time-resolved *in situ* XRD patterns show that the formation of an intermediate phase depends on the reduction conditions, such as the amount of hydrogen gas and heating rates.

Figure 1(a) shows the x-ray diffraction patterns of CuO and Cu₂O powder when they were reacted with hydrogen above 200 °C under normal flow (flow rate $> 15 \text{ cm}^3 \text{ min}^{-1}$). There is no hint of an intermediate phase, Cu_xO_y, during the reduction. Instead, Cu phase peaks appear

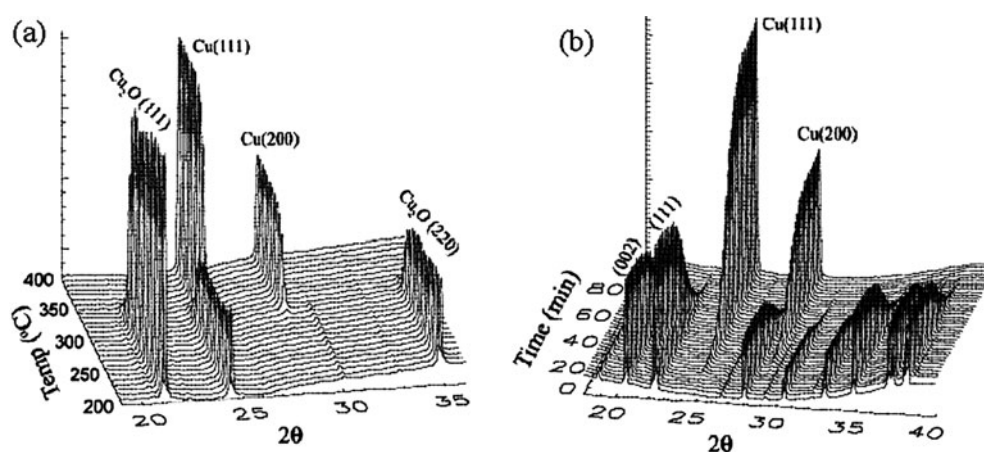


Figure 1. Synchrotron-based time-resolved *in situ* XRD patterns ($\lambda = 0.9147 \text{ \AA}$) during the reduction of Cu_2O powder by H_2 at variable temperature, 200–400 °C (a), and CuO at constant temperature, 200 °C (b).

and increase in intensity as CuO peaks decrease after an induction period, suggesting that Cu grains nucleate directly from CuO. The analysis of peak intensities at different temperatures shows that the reduction rate becomes slow and the induction period appears more significant as the isothermal temperature decreases (figure 1(b)). During this stage, it is believed that a few hydrogen atoms migrate into the bulk until favourable sites with a high efficiency for the adsorption of hydrogen are formed on the oxide surface. Once part of the H migrates into the bulk of CuO, hydroxo-like species are formed, and these are likely precursors for the removal of oxygen atoms as water.

It is worth noting that obtaining exactly the same reduction x-ray diffraction data is never an easy task, mainly due to the lack of information about the surface conditions, for example the homogeneity of the powder and number of pre-existing oxygen defects. Our studies revealed that the reduction process is also determined by other factors such as the hydrogen flow rate and temperature ramping condition. For example, the reduction behaviours of fresh powder are clearly different from the ones shown in the reduced/oxidized powder: powders reduced then oxidized require less induction period and a shorter reduction process time than fresh powders, illustrating a difference in the surface conditions, probably a different number of oxygen defect sites. Although calculations of activation energy and enthalpy of formation are difficult tasks due to the large error produced by the uncertainties described above, approximate values were estimated to be 0.66 and 1.19 eV for CuO and Cu_2O , respectively [9].

A series of refinements for the lattice constant, phase fraction and atomic configuration of the phases appearing during the reduction process was made from CuO powder using Rietveld analysis from the data obtained at the APS in a higher Q ($>10 \text{ \AA}^{-1}$). Refinements of the observed data were made based on a least-squares fit to the calculated scattering intensity using the GSAS program, which was also used to refine a new structure. As shown in figure 2(a), the measured data are in good agreement with the calculated patterns (wR_p , a 'goodness of the fit', is less than 1) using only CuO and Cu phases; no other phases are required. The grain sizes and oxygen occupancies of the powder during the reduction were obtained from a peak profile analysis [10], based on a full width at half maximum (FWHM) of the CuO(111) peak. The results show that the CuO grains stay constant in size (less than a micrometre), and do not lose much more oxygen than 10% before starting reduction (see figure 2(b)), which agrees with the

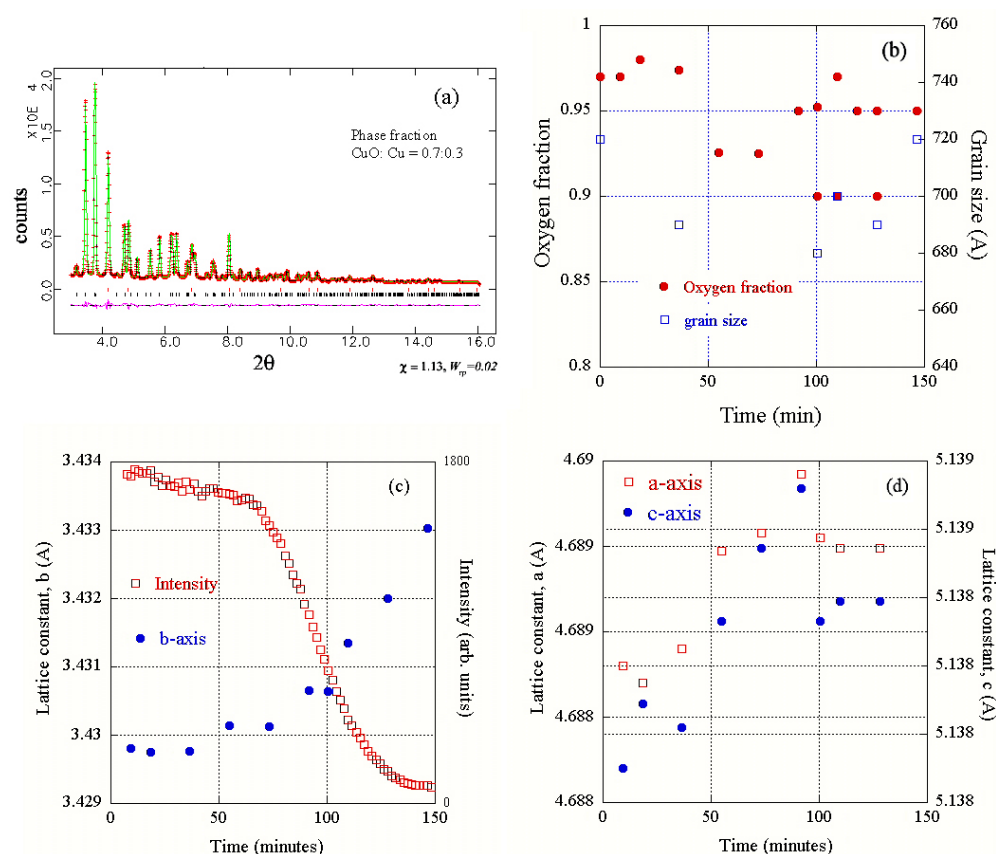


Figure 2. Plots for (a) GSAS refinement result fit to the x-ray diffraction data, (b) oxygen fraction, (c) grain sizes, and (d) lattice constants of the CuO phase during the reduction.

observation reported by Li *et al* [2] measured by depth profiling in a CuO thin film. The lattice constants of the phases do not change in a noticeable manner, except increasing 0.0007, 0.003, and 0.0005 Å for ‘a’, ‘b’ and ‘c’ directions, respectively (figures 2(c) and (d)). Combining these results suggests that the quality of CuO and Cu grains remains the same throughout the reduction process, and that the Cu grains nucleate first by removal of oxygen from the CuO matrix. The first-principles density functional calculations predict that embedded hydrogen atoms, estimated to be in a small concentration (probably $\text{Cu}_{16}\text{O}_{16}\text{H}_{<1}$), should expand the CuO lattice.

Reduction parameters such as the activation temperature, hydrogen flow rate, and temperature programmed reduction (TPR) conditions are expected to play a key role in understanding the reduction mechanisms. In fact, a reduction process is strongly influenced by the heating rate. Figure 3 shows time-resolved x-ray diffraction patterns when the CuO powder was reduced under different heating rates (from $10^\circ\text{C min}^{-1}$ to higher). No hint of an intermediate phase formation is observed during the reduction when the powder is heated at a rate smaller than $10^\circ\text{C min}^{-1}$ (figure 3(a)). When the TPR is increased to $20^\circ\text{C min}^{-1}$, however, a slight, but clear, hint of Cu_2O phase formation is observed, as indicated by the arrow in figure 3(b). At a higher heating rate ($40^\circ\text{C min}^{-1}$), the existence of the intermediate phase becomes clearer (figure 3(c)), and it constitutes nearly 40% in phase fraction when the heating rate is greater than $50^\circ\text{C min}^{-1}$ (figure 3(d)).

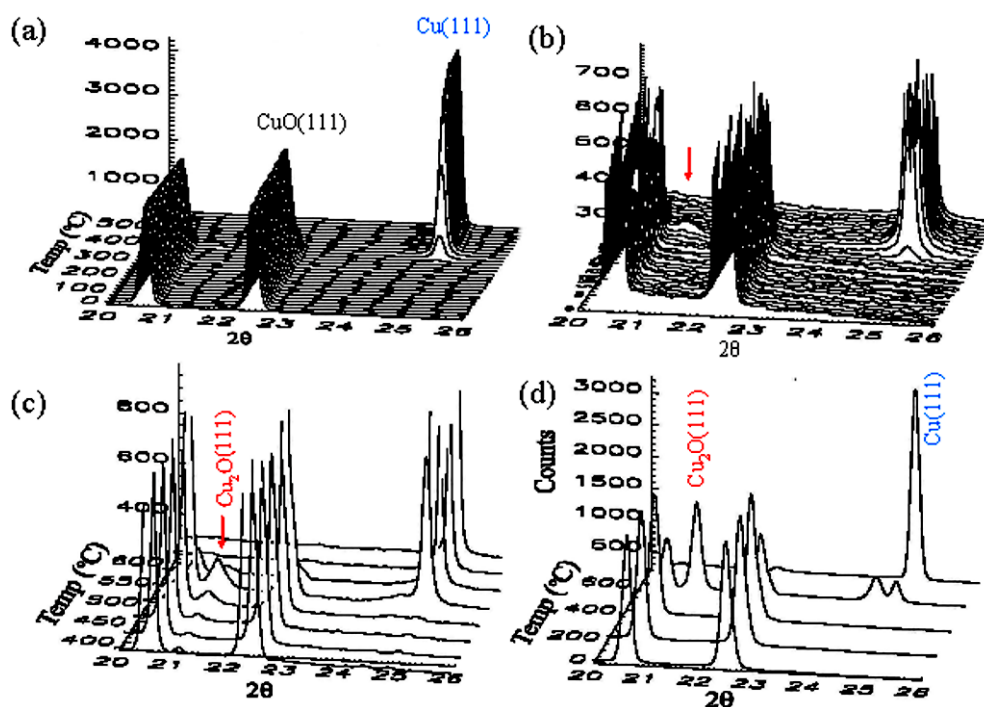


Figure 3. X-ray diffraction plots for the formation of Cu_2O phase when CuO powders are reduced at different heating rates: (a) $10\text{ }^\circ\text{C min}^{-1}$, (b) $20\text{ }^\circ\text{C min}^{-1}$, (c) $40\text{ }^\circ\text{C min}^{-1}$, and (d) greater than $50\text{ }^\circ\text{C min}^{-1}$. The Cu_2O peaks are indicated by arrows.

4. Conclusions

A detailed study of the reduction process of CuO and Cu_2O powders by hydrogen was performed using synchrotron-based time-resolved *in situ* x-ray diffraction measurements. The results demonstrated that, under a normal supply of hydrogen, CuO reduces directly to metallic Cu without the formation of intermediates or suboxides; this agrees with GSAS results refined from data obtained at high Q ($>10\text{ \AA}^{-1}$). When the CuO powders reacted with hydrogen under non-isothermal fast ramping conditions, however, the powders reduce through the intermediate phase (Cu_2O), and the appearance of the phase was more significant with increasing heating rate. The reasons for not observing the intermediate phases, such as Cu_2O and Cu_4O_3 phases, are still unclear. It is believed, however, that the intermediates are formed at the grain boundaries, which is not confirmed by XRD. The combined results of XRD for the studies of long range order and of EXAFS for the studies of short range order are expected to give a plausible explanation for the reduction process of this system.

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