JOURNAL OF CATALYSIS 83, 469–471 (1983)

NOTES

Oxidation States of Copper during Reduction of Cupric Oxide in Methanol Catalysts

INTRODUCTION

Reduction of cupric oxide by hydrogen in various catalyst systems has attracted considerable attention because of industrial applications (*1*, *2*) and for fundamental understanding of catalyst activation (*3*). Experimental techniques such as temperature programmed reduction (TPR) (*4*), hydrogen pressure drops (*5*), oxidation and reduction cycling (*6*), water production measurements (*7*), static X-ray diffraction (XRD) (*8*, *9*), and conductance measurements (*8*) have been used to study the reduction process. From these methods, the copper oxidation states were sometimes deduced.

An intermediate Cu_2O phase has been observed in copper (oxide)/alumina catalysts with low copper loadings (*10*). However, in pure or bulk CuO (*5*, *9*), bimetallic samples (*4*), and supported copper catalysts (with high copper loadings) (*5*, *9*), the intermediate was not detected. Indication of a second phase or reduction process was shown for doped CuO (*9*), and in pure CuO by conductance–XRD static measurements (*8*). The existence of a Cu^+ intermediate was shown to occur in copper containing zeolites by TPR (*11*) and by optical absorption and emission spectra (*12*).

In a current study of a copper/zinc oxide/alumina methanol catalyst, *in situ* XRD was used to study the reduction of $CuO/ZnO/Al_2O_3$ (60/30/10 wt%) and CuO/ZnO (67/33 wt%). XRD supplied information on relative reaction rates and direct determination of chemical structure throughout the reduction process.

EXPERIMENTAL

Catalyst samples were coprecipitated from copper, zinc, and aluminum nitrate salts by dropwise addition of sodium carbonate at 30°C until a pH of 6.9 was reached. The precipitates were dried at 90°C and subsequently calcined at 350°C for 4 h.

In situ XRD was performed in a 600-cm^3 steel reactor mounted on a General Electric XRD-5 using CuK_α radiation. It was equipped with external alignment controls, a 180° beryllium window, an inner heating block-sample holder, and variable temperature and feed gas controls. Powder samples were mounted in a 15 × 3-mm cylindrical hole inside the inner heating unit.

Reductions were carried out in 2 or 5% H_2 in N_2 at 250°C. A flow of 70 cm^3/min was maintained throughout the reductions. This provided a convenient time frame for analysis. The experimental apparatus was determined to be air tight because reoxidation of freshly reduced samples did not occur after extended periods under reaction conditions.

Various XRD peaks were used to monitor the course of the reaction. To aid in the identification of such peaks, Fig. 1 shows the fully reduced $CuO/ZnO/Al_2O_3$ catalyst—curve A, and a partially reduced CuO/ZnO mixture—curve B. XRD peaks were scanned approximately every 15 min at 2° 2θ/min. The intensities, which were approximated by peak heights, were converted to the respective weight percentages by the direct comparison method described by Cullity, a semiquantitative approach

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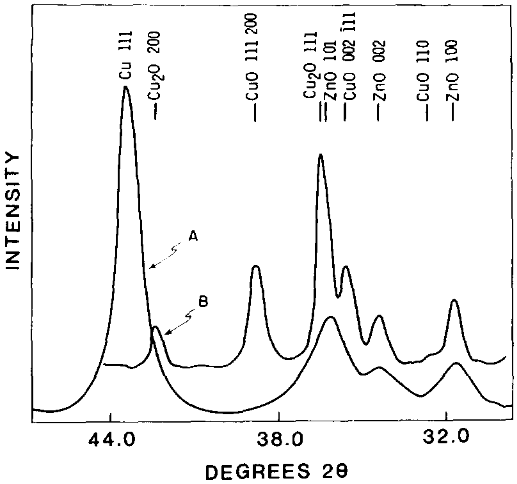

FIG. 1. XRD peak identification aid—curve A for a fully reduced catalyst and curve B for a partially reduced catalyst.

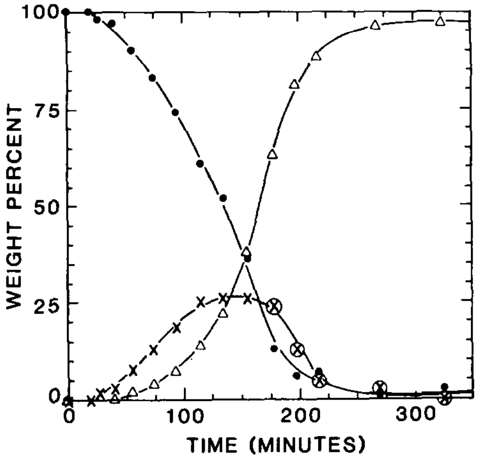

FIG. 2. Reduction profile for the $CuO/ZnO/Al_2O_3$ (60/30/10 wt%) catalyst given in terms of the wt% Cu (Δ), Cu_2O (×), extrapolated Cu_2O (⊗), and CuO (●). 70 cm^3/min of 2% H_2/N_2 at 250°C.

(*13*). Experimental conversion factors were determined from intensity ratios of standard mixtures containing Cu, Cu_2O, and CuO. The ratios for the Cu{111}/Cu_2O{200}, Cu{111}/CuO{111}{200}, and CuO{111}{200}/Cu_2O{200} reflections were used, which had the values of 2.90 ± 0.15, 2.94 ± 0.15, and 0.98 ± 0.05, respectively. These conversion factors were approximated as constant throughout the reductions.

RESULTS AND DISCUSSION

The $CuO/ZnO/Al_2O_3$ XRD reduction profile in 2% H_2 in N_2 is shown in Fig. 2. The CuO peak decreased as expected, and the intensity of the ZnO reflection was constant throughout the reaction. The Cu_2O intermediate initially formed quicker than metallic copper, but after about half the total reduction time the Cu peak increased much faster. The Cu_2O peak became masked as the Cu peak grew because of line broadening resulting in peak overlap. The Cu_2O concentration was extrapolated after the 160-min data point to maintain a material balance. This approximation was not necessary in the two-component sample as will be shown.

The CuO/ZnO reduction profile is shown in Fig. 3. The reaction was carried out in 5% H_2 (rather than 2% H_2) in N_2 to increase the reaction rate. Reduction of the three-component sample was performed for comparison. No difference other than reaction rate was observed, which was approximately five times faster, between reductions in 2 and 5% H_2.

In the two-component catalyst, Cu_2O acted as a definite intermediate, and metallic copper virtually did not form until all the CuO was reduced to Cu_2O. This shows the reduction proceeds preferentially from CuO to Cu_2O rather than from Cu_2O to Cu

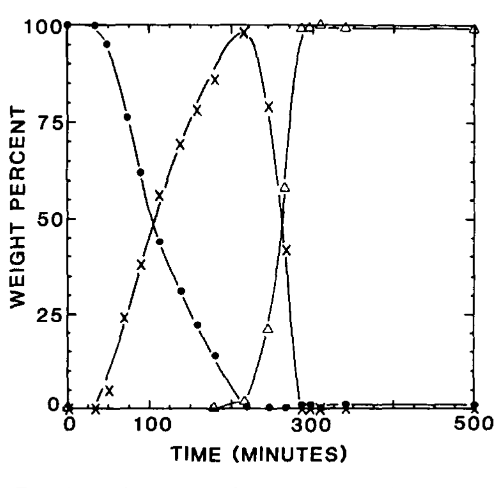

FIG. 3. Reduction profile for the CuO/ZnO (67/33 wt%) catalyst given in terms of the wt% Cu (Δ), Cu_2O (×), and CuO (●). 70 cm^3/min of 5% H_2/N_2 at 250°C.

or CuO to Cu. The intensity of the ZnO reflection was constant throughout the reduction.

An increase in reaction rate as a result of adding a high surface area (Al_2O_3) support has been documented (*5*). The effect was considered to be due to a high dispersion of the CuO. This is in agreement with transmission electron microscope studies of the present two systems. The CuO and ZnO crystallites in the $CuO/ZnO/Al_2O_3$ sample were in the range of 3 to 20 nm, and in the CuO/ZnO system, 25 to 100 nm with respective surface areas (BET-Ar gas) of 57 and 23 m^2/g (*14*). XRD showed only CuO and ZnO in both systems within an estimated error of 5 wt% for a crystalline phase. In the three-component sample, no diffraction effects were observed from the alumina which indicates the presence of an X-ray amorphous phase.

In a recent study of oxidation states of copper on alumina, the authors indicated that higher concentrations of intermediate Cu_2O formed when chemical copper oxide–alumina interactions occurred prior to reduction (*6*). In the present study only CuO was involved, and the intermediate was present in both cases. Cu_2O concentrations appeared to be higher in the sample without alumina, but this is most likely a result of the slower reaction rate rather than a different reduction mechanism.

The difference in the Cu_2O concentration during the reductions for the two systems can be related to the initial morphology of the CuO crystallites. In the alumina-containing sample, the crystals were about four times smaller, and the reaction rate was approximately six times faster.[1] In this case the reduction could go to completion in some crystals before the hydrogen reached all the crystals. With the larger crystals and slower reaction, this would not necessarily be the case. Both systems had residual CuO present after the given reduction times indicating that reduction had not quite reached equilibrium.

In summary, the reduction of CuO by hydrogen has been observed to go through an intermediate Cu_2O phase. The mechanism appears to be independent of crystallite size or dispersion, but the reaction rate is strongly dependent on these factors.

ACKNOWLEDGMENTS

The authors thank Dr. Kenneth R. Lawless for providing the *in situ* XRD reactor and for helpful discussions on copper oxidation states. The research was supported by the United States Department of Energy—Grant DE-AC05-796R10069.

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Received November 30, 1982; revised May 17, 1983

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[1] The CuO in the alumina sample was diluted by approximately 9 wt% compared to the CuO/ZnO sample. The effect of this relative to the comparison of the reduction rates is negligible.