

# Role of the Cu–Co alloy and cobalt carbide in higher alcohol synthesis

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## Abstract

Formation and decomposition of the Cu–Co alloy and  $\text{Co}_2\text{C}$  were studied using in situ X-ray diffraction (XRD), TG-DTA and TEM techniques. Cu–Co alloy with ratio Cu/Co = 1:1 has been obtained under treatment of  $\text{CuCoO}_2$  with hydrogen at 230–300°C.  $\text{Co}_2\text{C}$  was formed from Cu–Co alloy at 280–310°C and decomposed at 390–400°C under CO. It was shown that the role of Cu–Co alloy consisted in formation of cobalt carbide was able to activate CO undissociatively that led to oxygenates synthesis. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Cu–Co based catalyst; Cu–Co alloy; Higher alcohol synthesis; Cobalt carbide; In situ XRD

## 1. Introduction

Copper–cobalt based catalysts are selective for higher alcohol formation from syngas [1,2]. In our laboratory, we have undertaken a study in order to understand the nature of active sites in Cu–Co catalyst. For this purpose, we have prepared, characterized and evaluated precursors with various compositions (Cu–Co–Al, Cr, Zn, Mg). The behavior of the most active catalyst was studied in situ. We have shown [3–5] that  $\text{CuCoO}_2$  was one of the effective precursors.  $\text{CuCoO}_2$  possesses the delafossite-type structure including  $\text{Cu}^{+1}$  and  $\text{Co}^{+3}$  ions.  $\text{CuCoO}_2$  transformed to low-temperature Cu–Co alloy and cobalt carbide under stream of  $\text{CO} + \text{H}_2$ . Temperature range of higher alcohol formation coincides with temperature of  $\text{Co}_2\text{C}$  exist-

ing in this catalyst — 310–390°C. Hydrocarbons were the main products out of these temperatures where catalyst consists of only metal phases: Cu–Co alloy (< 300°C) or individual Cu and Co metals (> 390°C).

The objective of the present investigation was to determine the peculiarities of formation and destruction of Cu–Co alloy and  $\text{Co}_2\text{C}$  and to understand their role in higher alcohol synthesis.

## 2. Experimental

$\text{CuCoO}_2$  was prepared by decomposition of coprecipitated hydroxocompound at 490°C [3]. Catalyst was characterized by X-ray diffraction (XRD) using a Siemens (D-500) diffractometer with Cu  $\text{K}\alpha$  radiation and was examined by TEM with 2010 JEM microscope. High temperature in situ XRD experiments were performed

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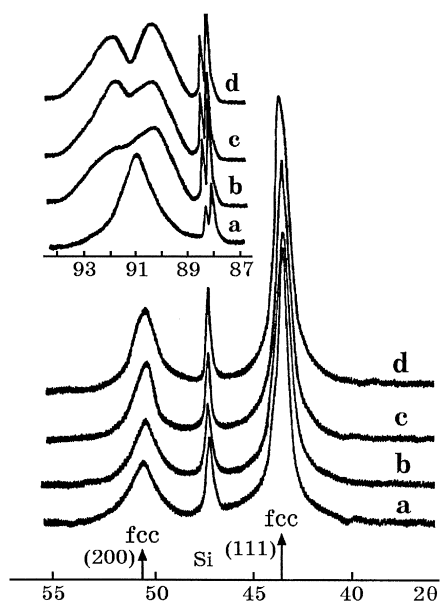


Fig. 1. XRD patterns for  $\text{CuCoO}_2$  treated with  $\text{H}_2$  at (a) 230°C, (b) 350°C, (c) 450°C and (d) 650°C.

using a reactor chamber [6]. A sample was heated (2°C/min) in  $\text{H}_2$  or  $\text{CO}$ , recording was performed after exposure at required temperature until the phase composition stopped changing. Thermal analyses (TG and DTA) were

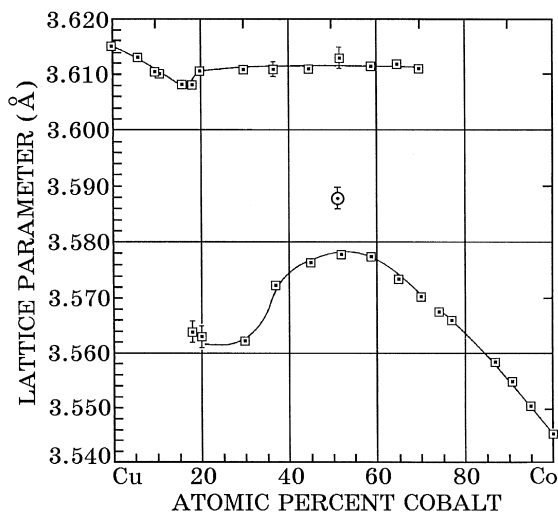


Fig. 2. Lattice spacing of fcc structures in quenched high-temperature (□) and low-temperature (○) Cu–Co alloys. Uncertainties in lattice spacing and composition are indicated by the dimensions of the symbols or by error bars.

carried out under  $\text{CO}$  flow with STA 409 Netzsch apparatus.

### 3. Results and discussion

#### 3.1. Formation and destruction of Cu–Co alloy

The XRD patterns for  $\text{CuCoO}_2$  treated with hydrogen are presented in Fig. 1. Diffraction lines attributed to only metal phase with face-centered cubic (fcc) lattice were observed. Line intensity increased with increasing of the reduction temperature. Precise examination of the line positions within the range  $2\theta = 85\text{--}95^\circ$  showed that lattice parameter of metal with fcc

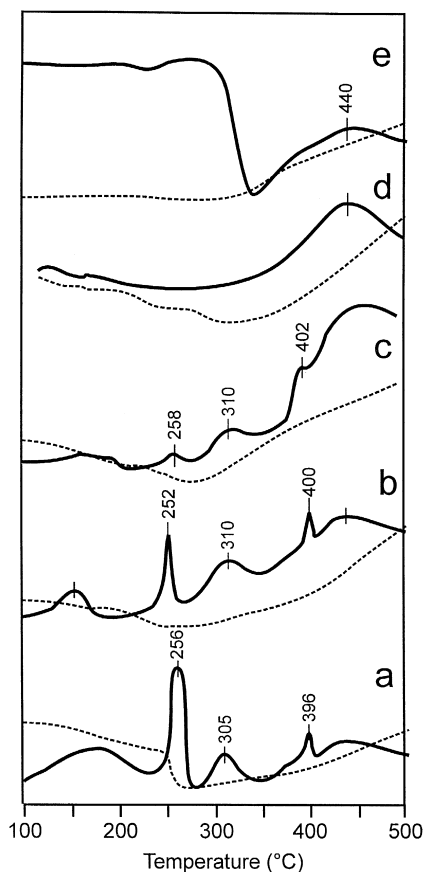


Fig. 3. DTA (solid lines) and TG (dashed lines) curves obtained under flowing  $\text{CO}$  for  $\text{CuCoO}_2$  pretreated with  $\text{H}_2$  at (a) 230°C, (b) 350°C, (c) 450°C, (d) 650°C, and for (e)  $\text{Co}_3\text{O}_4$ .

structure after treatment at 230°C is  $a = 3.587$  Å, that is less than lattice spacing for  $\text{Cu}^0$   $a = 3.615$  Å [7], and more than for  $\text{Co}^0$   $a = 3.557$  Å [8]. Hence, we can conclude that this metal is Cu–Co alloy. If we assume the statistic distribution of Cu and Co and the linear correlation between the changes in the lattice spacing and element content, the spacing  $a = 3.587$  Å will correspond to the alloy composition

$\text{Cu}_{0.5}\text{Co}_{0.5}$ . This alloy is stable up to 300°C. Particles of alloy are 100 Å in size. Increasing of the reduction temperature up to 350°C leads to line splitting. It means that two metal phase with fcc structure are formed — alloy with Cu/Co ratio  $\approx 4:1$  ( $a = 3.605$  Å) and  $\beta\text{-Co}^0$  ( $a = 3.557$  Å). After reduction at 450°C and 650°C, diffraction lines for two individual metal phases  $\text{Cu}^0$  and  $\beta\text{Co}^0$  were observed.

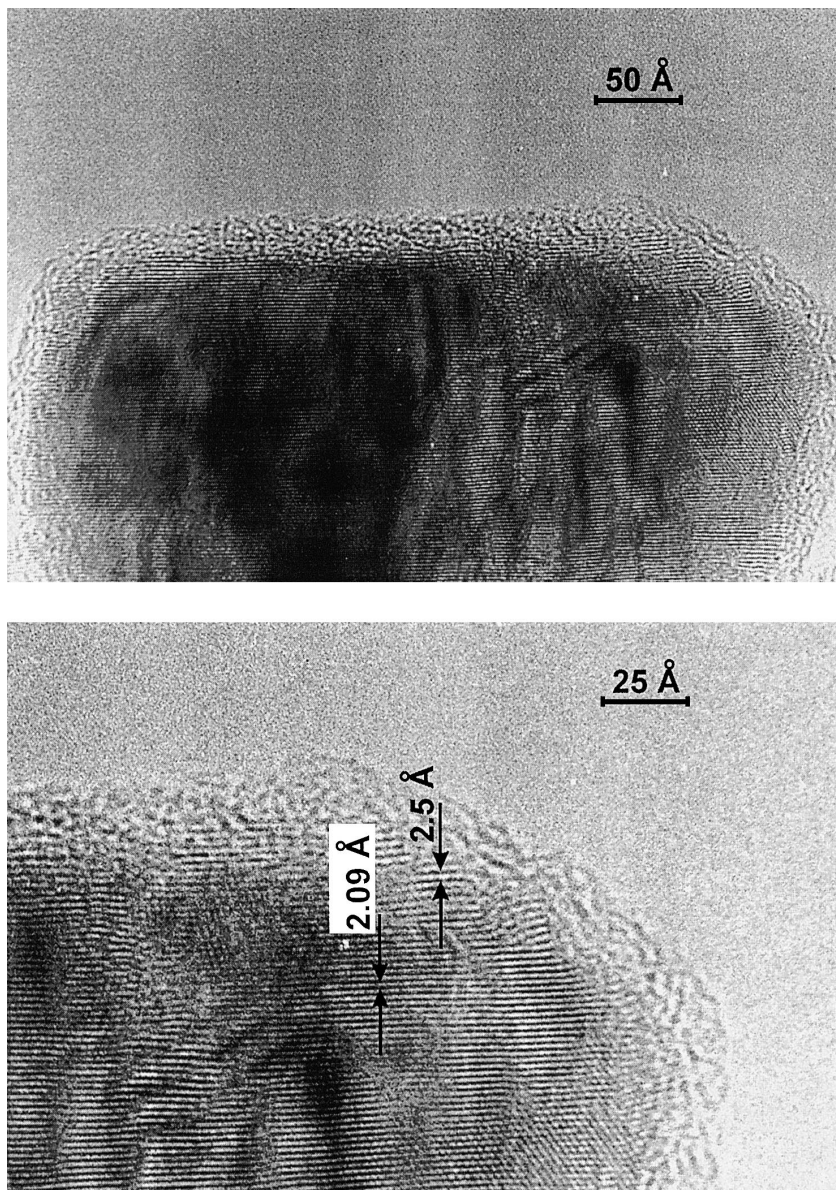


Fig. 4. TEM photographs of Cu–Co alloy after treatment with  $\text{CO} + \text{H}_2$  at 310°C.

Klement [9] showed that single-phase high temperature solid solution obtained by melting weighed quantities of the elements and quenching liquid alloys has the ranges 0–15 and 75–100 at.% Co–Cu. The inability to achieve complete solid solubility in Cu–Co alloys was explained by consideration of the rate processes during cooling and solidification. Fig. 2 presented lattice spacing of the fcc structures in quenched Cu–Co alloys [9] and low-temperature Cu–Co alloy obtained in present work by reduction of  $\text{CuCoO}_2$  at 230°C.

It can be concluded that low-temperature reduction of  $\text{CuCoO}_2$  allowed to obtain single-phase Cu–Co alloy with ratio Cu/Co = 1:1 that was impossible upon high temperature synthesis. The low temperature alloy was stable until 300°C. At temperature > 300°C  $\text{Cu}^0$  released from Cu–Co alloy. According to XRD data, two individual metal phases Cu and Co were detected at 450°C. Complete decomposition of Cu–Co alloy was observed only at 650°C as it is shown below.

### 3.2. Formation and destruction of cobalt carbide

$\text{CuCoO}_2$  prereduced at 230–650°C and  $\text{Co}_3\text{O}_4$  were characterized by thermal analyses under flowing CO (Fig. 3). Similar thermal behavior is observed for  $\text{CuCoO}_2$  pretreated at 230–450°C (Fig. 3a–c). A strong exotherm and weight loss occurs at 250–260°C due to reduction of the samples. Two exothermic transformations are apparent between 280°C and 400°C corresponding to formation (280–310°C) and decomposition (390–400°C) of the cobalt carbide. The weight growth above 400°C is attributed to carbon formation. In comparison with thermal curves of these samples, the  $\text{Co}_3\text{O}_4$  and  $\text{CuCoO}_2$  after reduction at 650°C (Fig. 3d–e) exhibit only one broad exothermic peak and weight growth corresponding to formation of carbon. So, formation of cobalt carbide was not observed for Cu–Co catalysts prereduced at

650°C and also for Co catalyst at the same experimental conditions.

The  $\text{CuCoO}_2$  treated with CO +  $\text{H}_2$  at 310°C was studied by high-resolution electron microscopy (Fig. 4). According to XRD, two phases exist in this sample — Cu–Co alloy and cobalt carbide. It can be seen from Fig. 4 that surface phase with the inter-plane distance of 2.50 Å is localized on the particles of the Cu–Co alloy ( $d = 2.09$  Å). The distance 2.50 Å is in a good agreement with the inter-plane distance of  $\text{Co}_2\text{C}$  — 2.42 Å. The contact of

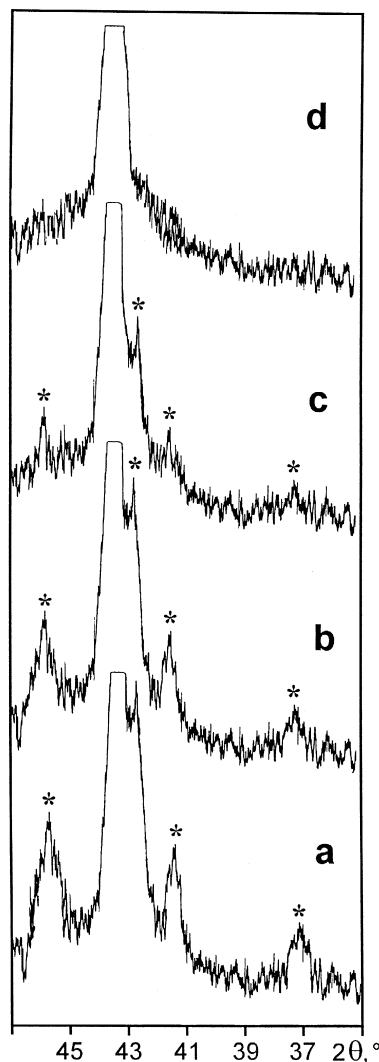


Fig. 5. XRD patterns for  $\text{CuCoO}_2$  treated with CO at 350°C after reduction in  $\text{H}_2$  at (a) 230°C, (b) 350°C, (c) 450°C and (d) 650°C; \* -  $\text{Co}_2\text{C}$ .

carbide phase with the surface of alloy particles proceeds with no change of parallelity of atomic planes of the coherent phases. Destruction of cobalt carbide is in time with decomposition of Cu–Co alloy. We can suggest that Cu–Co alloy under CO + H<sub>2</sub> exists as long as carbide, which covers it, exists. As soon as carbide decomposes, the surface of the alloy becomes accessible for CO + H<sub>2</sub> and the alloy is decomposed to its elements — copper and cobalt metals.

Verification of the above thermal assignment is provided by the XRD patterns for CuCoO<sub>2</sub> after treatment with CO at 350°C. As shown by XRD patterns in Fig. 5, diffraction lines at 2.42, 2.17, 2.11, and 1.98 Å attributed to the Co<sub>2</sub>C [10] appear for catalyst pretreated at 230°C, 350°C and 450°C along with lines of the metal with fcc structure. Carbide phase was not observed for sample pretreated at 650°C. Formation of Co<sub>2</sub>C with detectable rate was observed only from Cu–Co alloy, even if Cu in alloy was in minor amount (for sample pretreated at 450°C). These results are in good agreement with Hofer and Peebles [11] who noted that reaction between CO and finely divided cobalt was very slow under atmospheric pressure and 250–350°C, and required more than 500 h to come to completion. From our results, it follows that the rate of carbide formation increases in the presence of copper.

Thus, the role of Cu–Co alloy consists in formation of cobalt carbide. As we have shown earlier [4], the appearance of the carbide phase or surface carbide results in the alcohol formation. The amount of carbide phase increases as

temperature increases, the alcohol productivity also grows and reaches its maximum at 330–350°C. Decomposition of the cobalt carbide and Cu–Co alloy under CO + H<sub>2</sub> at 390–400°C takes place simultaneously with the catalyst deactivation in relation to alcohol synthesis. According to the well-known scheme [1,2], the higher alcohol synthesis requires two types of CO activation which proceeds by undissociative and dissociative ways. In our case, metal phases — Co<sup>0</sup> and/or Cu–Co alloy were responsible for CO dissociation and formation of surface C<sub>n</sub> (n ≥ 1) species. Co<sub>2</sub>C has been proposed as able to activate CO without rupture and insert CO into C<sub>n</sub> species that led to higher alcohol synthesis.

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