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THERMAL STABILITY OF $CuO–Al_2O_3$ SYSTEM DOPED WITH SODIUM

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ABSTRACT

Copper–aluminium mixed oxide was prepared by impregnation of γ-Al_2O_3, preheated at 400 ° C, with copper nitrate solution in an equimolecular ratio. Three samples of $CuO–Al_2O_3$ doped with Na^+ (2, 5 and 10% Na^+) were prepared by the addition of NaOH solution of the appropriate concentration to the solid $CuO–Al_2O_3$ preheated to 400 ° C. The thermal decomposition of different mixed oxides was studied using DTA. The X-ray spectra of the thermal products of the pure and mixed oxides were also studied.

The results obtained revealed that the thermal treatment of solid $CuO–Al_2O_3$ at 500 ° C produced only a crystalline form of CuO. At 800 ° C the degree of crystallinity of CuO was increased and a new phase, $CuAl_2O_4$ spinel, appeared. Further increase in the temperature led to the disappearance of CuO and the formation of a $CuAlO_2$ phase.

The introduction of sodium ions (2%) into the mixed oxide and heating the solid at 1000 ° C showed a marked decrease in the degree of crystallinity of the monovalent copper complex $CuAlO_2$ with the increase of the divalent copper aluminate $CuAl_2O_4$ spinel. Moreover the addition of 5% Na^+, or more, caused completely different behaviour, i.e. a sharp decrease in the degree of crystallinity of both $CuAlO_2$ and $CuAl_2O_4$ phases with a marked increase of a well-defined crystalline CuO phase. The mechanism of the sodium doping of the $CuO–Al_2O_3$ solid is discussed.

INTRODUCTION

The binary oxides are widely used in catalysis [1–4]. One of the most important catalysts used in many chemical reactions is the copper–alumina system [5–7]. Several investigations have been reported dealing with a number of properties of this system [8–10]. Wolberg et al. [11] studied the X-ray, and K-absorption edge spectroscopy of samples containing cupric ions supported on η-alumina. They identified three distinguishable phases in

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composites containing cupric ions dispersed on alumina; isolated cupric ions, a copper aluminate surface phase and cupric oxide. They also found that the aluminate phase was detectable even on material calcined at temperatures as low as 300 ° C. Pierron et al. [12] applied in situ X-ray diffraction and differential thermal analysis to study a $CuO-Al_2O_3$ catalyst during a CO-oxidation reaction. They found that the X-ray spectra under reaction conditions differ from these obtained at ambient conditions. Friedman et al. [13] using ESCA reported that an aluminate phase was observed in samples containing less than 4% CuO while a free CuO phase was obtained on samples containing more than 4% CuO. From these investigations it can be concluded that the copper–alumina catalyst is a complex system and the aluminate spinel was not observed at high temperature but appears on material calcined at temperatures as low as 300 ° C. This investigation has studied the thermal decomposition of the $CuO-Al_2O_3$ system and the effect of sodium ions on its thermal stability.

EXPERIMENTAL

Preparation of samples

Pure aluminium oxide was obtained by adding a dilute ammonia solution to aluminium nitrate solution at 70 ° C with stirring until pH 7 was reached. The precipitate was filtered off and washed until free of NO_3^- ions. The solid was dried at 110 ° C for 6 h and calcined at 550 ° C in air for 5 h. Copper–aluminium mixed oxide was prepared by impregnation, from aluminium oxide and copper nitrate solution in an equimolecular ratio. The dried solid was heated at different temperatures (500, 800 and 1000 ° C) for 4 h in air. Three $CuO-Al_2O_3$ samples containing 2, 5 and 10% Na^+ ions were prepared by adding the calculated sodium hydroxide solution to the solid $CuO-Al_2O_3$ preheated at 500 ° C and the materials obtained were dried at 110 ° C and subjected to thermal treatment at 1000 ° C.

Techniques

Differential thermal analysis (DTA) of the pure and mixed oxides and copper nitrate was carried out using a Du Pont 900 thermal analyser with a differential scanning calorimeter cell. The rate of heating was 10 ° C min^{-1}.

An X-ray investigation of the thermal products of pure CuO, Al_2O_3, $CuO-Al_2O_3$ and the solids treated with sodium hydroxide was performed with a Philips diffractometer (type PW 1051). The patterns were obtained using nickel-filtered copper radiation ($\lambda = 1.5405$ Å) at 36 kV and 16 mA; the diffraction angle 2θ was scanned at a rate of 2° min^{-1}.

RESULTS

Characterization of individual copper and aluminium oxides

The DTA of copper nitrate revealed that the thermal treatment of this salt yields CuO above 300 ° C. From the DTA curve (Fig. 1), it can be observed that at 200–300 ° C an endothermic peak occurred due to the elimination of water of crystallization and the decomposition of copper nitrate. At about 950 ° C another endothermic peak was observed due to the decomposition of CuO leading to the formation of Cu_2O

$$2CuO \rightarrow Cu_2O + O \tag{1}$$

whereas the DTA curve of Al_2O_3 preheated to 550 ° C (Fig. 1) showed no detectable change between 500 and 1000 ° C.

Characterization of copper–aluminium mixed oxides

The DTA of the impregnated Al_2O_3 is illustrated in Fig. 1. A broad endothermic peak between 200 and 400 ° C due to the decomposition of copper nitrate was observed. Another exothermic peak at a temperature higher than 1000 ° C was also detected. This exothermic peak may be attributed to the decomposition of the $CuAl_2O_4$ spinel formed (not detected

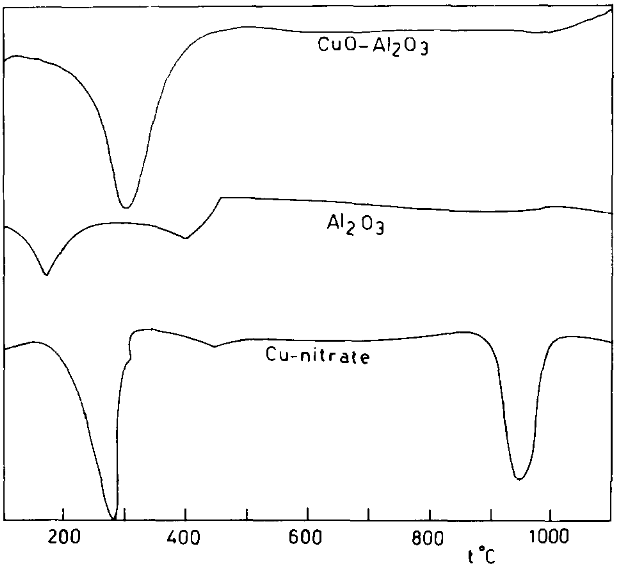

Fig. 1. DTA of copper nitrate, hydrated Al_2O_3 and the Cu-impregnated alumina.

on the DTA curve) thus producing $CuAlO_2$. The processes may be represented as follows

1. Formation of spinel

$$CuO + Al_2O_3 \xrightarrow{700-900\,^\circ C} CuAl_2O_4 \tag{2}$$

2. Decomposition of spinel

$$2CuAl_2O_4 \xrightarrow{1000\,^\circ C} 2CuAlO_2 + Al_2O_3 + O \tag{3}$$

Figure 2(a) illustrates X-ray diffraction patterns of the products of thermal treatment of $CuO-Al_2O_3$ at different temperatures. It can be seen that at 500 °C only the CuO crystalline phase was detected. The solid heated at 800 °C showed two distinct phases (CuO and $CuAl_2O_4$). However, at such a temperature the degree of crystallinity of CuO increased and at the same time $CuAl_2O_4$ spinel was formed according to eqn. (2). The X-ray diffraction pattern of the thermal product of $CuO-Al_2O_3$ heated at 1000 °C revealed that this solid consisted mainly of $CuAlO_2$, and some $CuAl_2O_4$ spinel (eqn. 3).

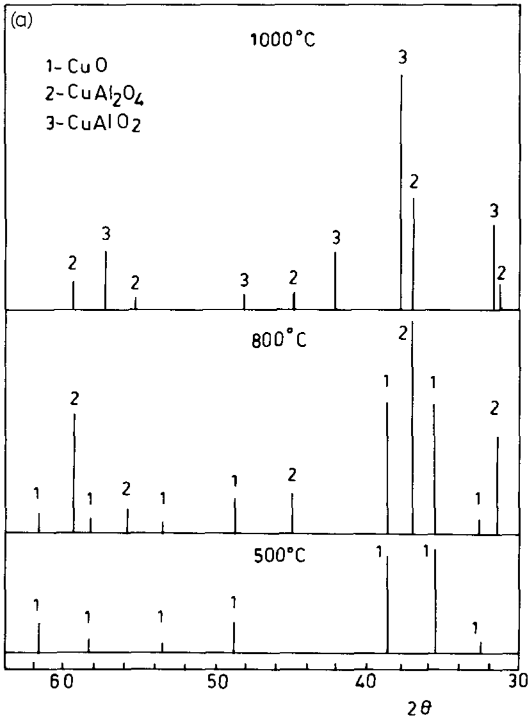

Fig. 2(a). X-ray diffraction patterns of the products of thermal treatment of $CuO-Al_2O_3$ at 500, 800 and 1000 °C.

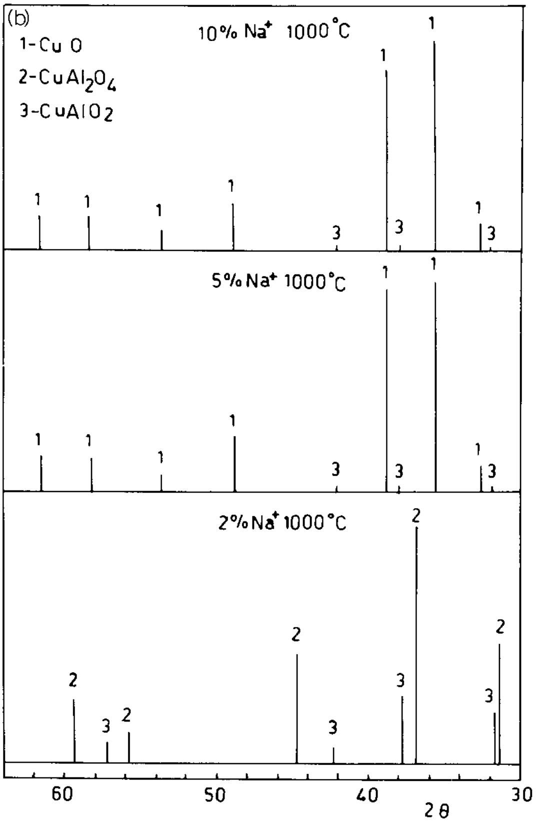

Fig. 2(b). X-ray diffraction patterns of the products of thermal treatment of CuO–Al_2O_3 doped with sodium ions at 1000 ° C.

Characterization of copper–aluminium mixed oxides doped with sodium ions

These results revealed that the thermal treatment of solid CuO–Al_2O_3 at 1000 ° C produced mainly $CuAlO_2$. The addition of 2% Na^+ ions to the CuO–Al_2O_3 sample and heating at 1000 ° C for 4 h produced a solid containing mainly $CuAl_2O_4$ spinel (Fig. 2(b)) in contrast with the solid heated without Na^+. The 5% Na^+-treated sample heated at 1000 ° C showed the disappearance of both the $CuAl_2O_4$ and $CuAlO_2$ phases and the patterns detected belonged to the crystalline CuO phase only. The incorporation of 10% Na^+ in the CuO–Al_2O_3 system had more or less the same effect as in the case with 5% Na^+. These results showed the tendency of sodium ions to stabilize the CuO crystal lattice in the Al_2O_3 phase without any reaction even at 1000 ° C (Fig. 2(b)).

DISCUSSION

The DTA curve of basic copper nitrate showed an endothermic peak between 200 and 300 °C due to the decomposition of the nitrate into cupric oxide. The formation of cuprous oxide from cupric oxide seemed to be an endothermic process at 900–1000 °C. The thermal treatment of $CuO-Al_2O_3$ up to 900 °C showed no detectable change in the DTA. It was reported that the formation of $CuAl_2O_4$ spinel occurs in the temperature range 700–800 °C and is an exothermic process. This reaction was not observed in the DTA curve probably due to the very slow rate of formation. At higher temperature this spinel is not stable and it decomposes yielding $CuAlO_2$.

The study of the $CuO-Al_2O_3$ system is considered to be very important especially in the field of catalysis where the CuO phase is the most active and valuable species for certain catalytic processes. The thermal treatment of this system from the preparation stage up to 1000 °C proceeds via several processes. The composition of the product will depend greatly upon the final temperature of the thermal treatment.

The incorporation of sodium ions (2%) in the mixed oxides stabilized most of the $CuAl_2O_4$ spinel in the crystalline form. In this case a small amount of crystalline $CuAlO_2$ phase was also detected. In other words the presence of sodium ions in the mixed oxides stabilized the divalent Cu^{2+} in the spinel form and thus prevented the process of decomposition into $CuAlO_2$ i.e. reduction to Cu^+. The introduction of 5% or more sodium ions to the mixed oxides led to the fixation of the divalent state of copper in the form of crystalline phase of cupric oxide even at temperatures as high as 1000 °C. This can be attributed to the dissolution of sodium ions in the CuO lattice. The substitution of cuprous ions by Na^+ is geometrically possible due to the similarity between the ionic radii of Cu^+ and Na^+ (0.98 Å for both Cu^+ and Na^+). The introduction of Na^+ ions in the CuO lattice may be simplified [12,14] to give

$$Na_2O + \tfrac{1}{2}O_2(g) \rightarrow 2Na^+(Cu^+) + 2Cu^{2+}$$

($Na^+(Cu^+)$ denotes monovalent Na^+ ions located in the position of the host cations Cu^+ in the CuO lattice). This reaction is accompanied by fixation of atmospheric oxygen, and therefore the copper ions will be in the higher valency state. The absence of $CuAl_2O_4$ spinel in our case may be attributed to the reaction of sodium ions with alumina forming sodium aluminate thus preventing the migration of copper ions to the bulk of Al_2O_3 to form $CuAl_2O_4$ spinel; consequently in the X-ray diffractogram the lines of well-defined crystalline CuO phase were the only ones observed.

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