

THERMAL SOLID–SOLID INTERACTION BETWEEN CuO AND PURE Al₂O₃ SOLIDS

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ABSTRACT

Pure finely powdered aluminium hydroxide specimens were treated with solutions containing different proportions of cupric nitrate, followed by drying at 100 °C and roasting in air at temperatures varying between 500 and 1100 °C. The solid–solid interactions between the resulting mixed oxides were investigated using DTA, TG, DTG and X-ray diffraction techniques.

The results obtained revealed that cupric nitrate and aluminium hydroxide decompose readily at 250 and 320 °C respectively, to produce CuO and Al₂O₃ solids. The mixed oxides formed begin to interact at 650 °C, yielding CuAl₂O₄. The crystallinity of the resulting aluminate increases with increasing firing temperature up to 1000 °C, and remains thermally stable up to 1100 °C in the presence of excess alumina, then partially decomposes to CuAlO₂, in the case of a stoichiometric mixture of CuO and Al₂O₃. When the Al(OH)₃ specimen was roasted in air at 1000 °C, it yielded a mixture of κ - and θ -Al₂O₃ of moderate crystallinity; when fired at 1100 °C, a mixture of κ -, θ - and α -Al₂O₃ phases is produced. However, the presence of CuO (16.3 wt.%) results in the formation of well crystallized α -Al₂O₃ (corundum) at a temperature of about 1000 °C. The transformation of different aluminas into α -Al₂O₃ was found to be accompanied by an exothermic peak in the DTA curve at 975 °C.

INTRODUCTION

γ -Aluminas act as active catalysts for the dehydration reactions of some organic compounds [1–5]. However, they are commonly employed as catalyst supports for a large variety of metal and/or metal oxide catalysts used in several chemical reactions [6–12]. The choice of these solids as catalyst supports is based on the fact they greatly increase the degree of dispersion of the catalytically active constituents, hindering their grain growth and thus increasing the activity and durability of the supported catalysts [9,13].

The thermal treatment of $\gamma\text{-Al}_2\text{O}_3$ at elevated temperatures effects its conversion into other alumina phases such as the θ , κ and α forms [14–16]. These phases are sintered solids and could not be successfully employed as catalyst supports. Indeed, metal- or metal oxide-support interaction might take place during the thermal treatment of the supported catalysts. This solid–solid interaction results in the formation of the corresponding metal aluminate, which is not desirable in certain catalytic reactions [12]. The interaction between metal oxides and the Al_2O_3 support is, however, dependent on the history of the solids used, on the calcination conditions, on the extent of the loaded metal oxide and on the presence of small amounts of certain oxide impurities [14,17,18]. The metal oxide–support interaction can be monitored by several techniques, namely DTA, X-ray diffraction (XRD), IR, X-ray photospectroscopy, diffuse reflectance spectroscopy (DRS) and ion scattering spectroscopy (ISS) [12,16,17].

The present investigation was devoted to studying the effects of the chemical composition and of the calcination temperature on the mutual solid–solid interaction between CuO and Al_2O_3 . The techniques employed were DTA, TG, DTG and XRD.

EXPERIMENTAL DETAILS

Materials

Three specimens of cupric/aluminium mixed oxides with different compositions were prepared by impregnating finely powdered $\text{Al}(\text{OH})_3$ with solutions containing different proportions of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. These chemicals were of analytical grade and supplied by Prolabo and Fluka companies, respectively. The impregnated solids were dried at 100°C then roasted in air at $500\text{--}1100^\circ\text{C}$ for 6 h. The nominal compositions of the solids roasted at 500°C were $0.25\text{CuO} : \text{Al}_2\text{O}_3$, $0.5\text{CuO} : \text{Al}_2\text{O}_3$ and $\text{CuO} : \text{Al}_2\text{O}_3$. These solids are designated **CuAl-I**, **CuAl-II** and **CuAl-III** respectively.

Techniques

DTA, TG and DTG analyses of the impregnated solids were carried out using a Netzsch–Gerätebau thermal analysis apparatus (STA 405, type 6.223). The rate of heating was kept at $10^\circ\text{C min}^{-1}$. A 50 mg sample of solid specimen was used in each case.

An X-ray investigation of the thermal products of the various solids was carried out using a Philips diffractometer (type PW 1390). The patterns were run with nickel-filtered copper radiation ($\lambda = 1.5405\text{\AA}$) at 36 kV and 16 mA with a scanning speed of $2^\circ \text{ deg in } 2\theta \text{ min}^{-1}$.

RESULTS AND DISCUSSION

Thermal behaviour of different mixed solids

Figures 1 and 2 illustrate DTA, TG and DTG curves of the $\text{Al}(\text{OH})_3$ specimens impregnated with various proportions of cupric nitrate solution. Three endothermic peaks are observed in the DTA curves of the investigated solids. The maxima of these peaks are located at 250, 320 and 650 °C. The area of the first peak increases with increasing amounts of cupric nitrate; the second peak has almost the same area. The first two peaks are strong and sharp while the third peak is weak and broad. The first peak is accompanied by weight losses of 7.5, 10 and 15.2% for the solids designated CuAl-I, CuAl-II and CuAl-III respectively. The second peak is followed by weight losses of 18.5, 18.5 and 9.8%, for the same respective solids. The DTA curve of the CuAl-I solid has an additional exothermic peak at 975 °C which is not followed by any change in weight. It can be seen from Fig. 2 that CuAl-I, CuAl-II and CuAl-III solids lose 6, 4.4 and 2.5 wt.% respectively, by heating at temperatures varying between 400 and 600 °C. These weight losses might be attributed to the dehydroxylation of the Al_2O_3 produced [16]. In fact, it has been reported by some authors [13,16] that the complete removal of OH groups bound to Al_2O_3 solid requires a thermal treatment at temperatures

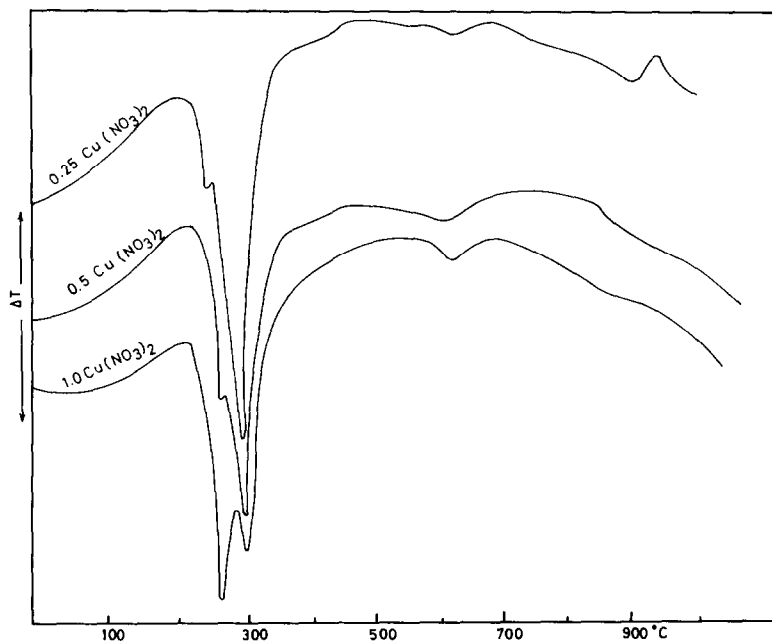


Fig. 1. DTA curves of $\text{Al}(\text{OH})_3$ specimens impregnated with 0.25, 0.5 and 1.0 mol $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ per mol Al_2O_3 .

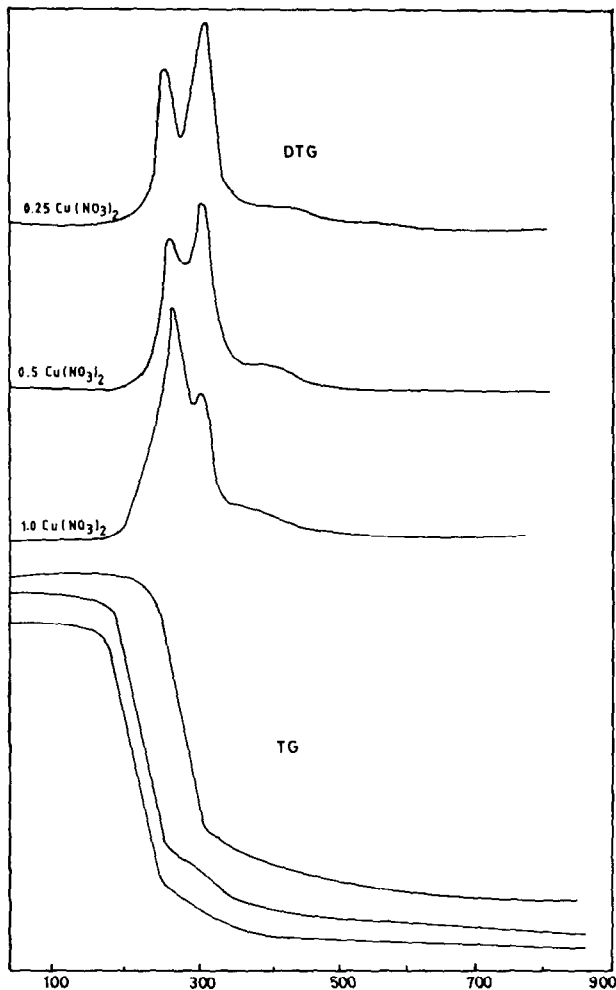


Fig. 2. TG and DTG curves of $\text{Al}(\text{OH})_3$ samples treated with 0.25, 0.5 and 1 mol cupric nitrate per mol Al_2O_3 .

above 450°C . The first peaks at 250°C might correspond to the thermal decomposition of cupric nitrate yielding CuO and the second peaks to the dehydration of aluminium hydroxide to produce Al_2O_3 . The third endothermic peaks at 650°C , not accompanied by any change in weight, might indicate solid–solid interaction between CuO and Al_2O_3 and/or phase transformation of the Al_2O_3 solid. Similarly, the exothermic peak at 975°C observed only in the DTA curve of the CuAl-I solid, which was not followed by any change in weight, might characterize solid–solid interaction or, more probably, a phase transformation process. These speculations may be verified with an XRD investigation of the various solids precalcined in air at varying temperatures.

XRD investigation of pure $\text{Al}(\text{OH})_3$ precalcined in air at different temperatures varying between 500 and 1100 °C

Preliminary experiments showed that $\text{Al}(\text{OH})_3$ preheated in air at temperatures below 700 °C was an amorphous solid. A poorly crystalline $\gamma\text{-Al}_2\text{O}_3$ was formed by heating the parent hydroxide at 900 °C. Figure 3 shows the diffraction patterns of $\text{Al}(\text{OH})_3$ precalcined in air at 900, 1000 and 1100 °C. It can be seen from this figure that Al_2O_3 -1000 °C is a mixture of θ - and $\kappa\text{-Al}_2\text{O}_3$ and has moderate crystallinity. The comparison of the relative intensities (I/I_0) of different diffraction lines suggests that $\theta\text{-Al}_2\text{O}_3$ is more abundant than $\kappa\text{-Al}_2\text{O}_3$. The increase in the firing temperature up to 1100 °C resulted in a slight improvement in the crystallinity of the θ and κ phases and led to the formation of $\alpha\text{-Al}_2\text{O}_3$ (corundum). These results clearly indicate that the complete transformation of different alumina phases into the α phase required a prolonged heating of pure Al_2O_3 solid at temperatures above 1100 °C. These findings are in good agreement with those reported by some investigators [17].

XRD of $\text{Al}(\text{OH})_3$ impregnated with different proportions of cupric nitrate and precalcined in air at 500–1100 °C

Figures 4–9 show the X-ray diffractograms of CuAl-I, CuAl-II and CuAl-III solids precalcined at 500, 700, 900, 1000 and 1100 °C. The diffrac-

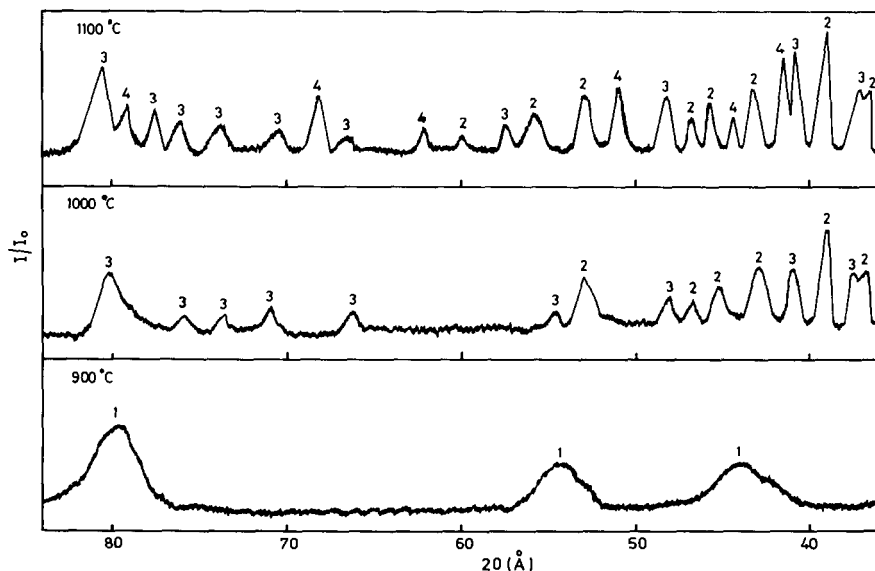


Fig. 3. X-ray diffractograms of $\text{Al}(\text{OH})_3$ heated at 900, 1000 and 1100 °C: lines (1) $\gamma\text{-Al}_2\text{O}_3$; lines (2), $\theta\text{-Al}_2\text{O}_3$; lines (3), $\kappa\text{-Al}_2\text{O}_3$; lines (4), $\alpha\text{-Al}_2\text{O}_3$.

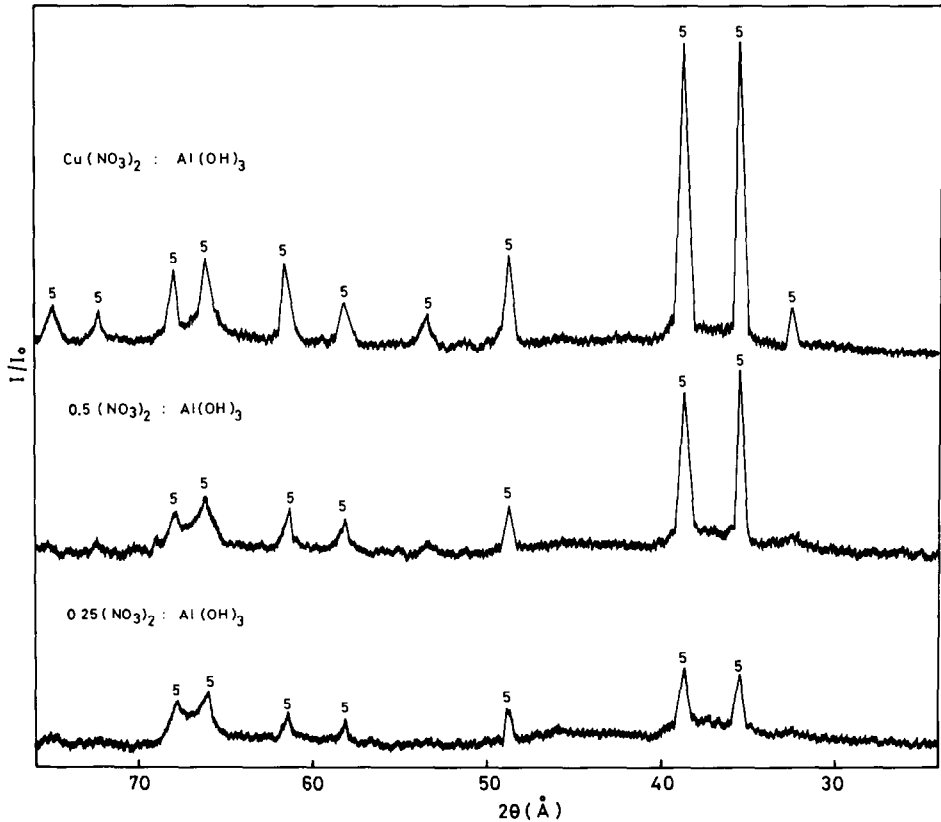
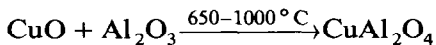


Fig. 4. X-ray diffractograms of CuAl-I, CuAl-II and CuAl-III fired at 500 °C: lines (5), CuO.

tion lines of the CuO phase only were detected in the patterns of all the mixed solids fired at 500 °C, indicating the absence of any solid–solid interaction between CuO and the amorphous Al₂O₃ solid at this temperature. Figure 5 shows that only the diffraction lines of CuO and CuAl₂O₄ were observed in the patterns of all the mixed solids precalcined at 700 °C. It can be concluded that the endothermic peaks at 650 °C detected in the DTA curves of the various solids investigated correspond to solid–solid interaction between CuO and Al₂O₃ yielding copper aluminate according to



The presence of free cupric oxide in all the mixed solids preheated at 700 °C suggests that this solid–solid interaction requires higher temperatures (> 700 °C) to reach completion. Figure 6 reveals that raising the firing temperature to 800 °C resulted in an important increase in the relative intensities of all the lines of the copper aluminate phase produced. These diffraction lines only were detected in the patterns of CuAl-I solid preheated at 800 °C. The rise in firing temperature to 900 °C also led to an important

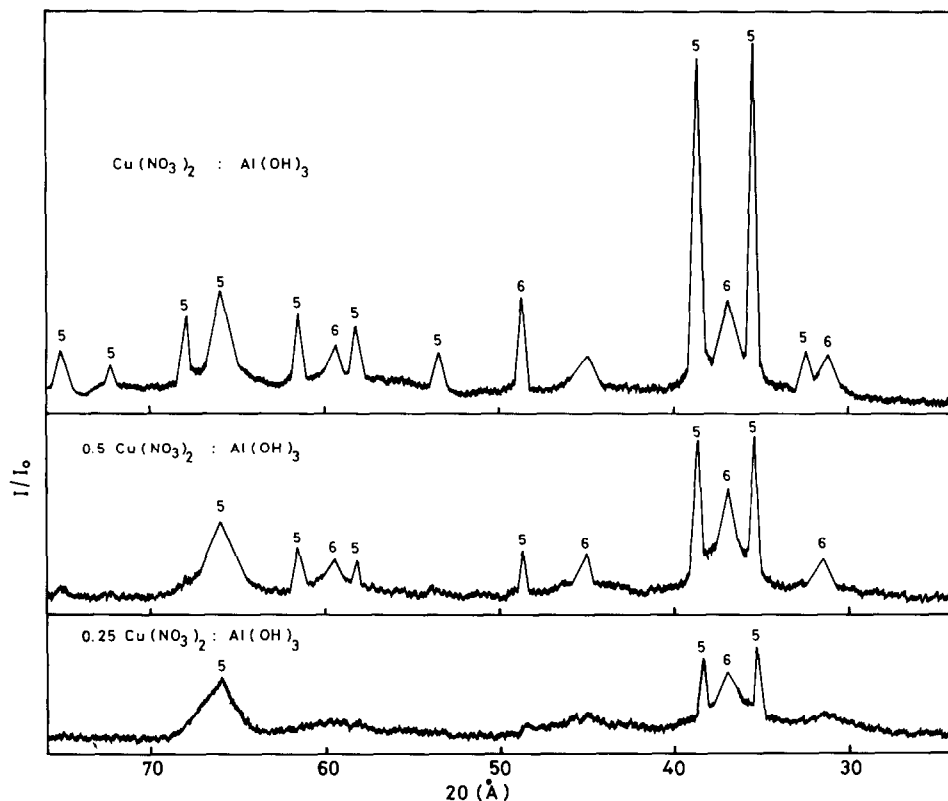
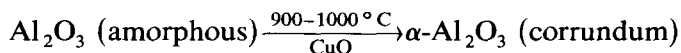


Fig. 5. X-ray diffractograms of CuAl-I, CuAl-II and CuAl-III heated in air at 700 °C: lines (5), CuO; lines (6), CuAl₂O₄.

increase in the crystallinity of the produced copper aluminate phase with subsequent appearance of small amounts of α -Al₂O₃ (c.f. Fig. 7).

The further increase in the pretreatment temperature of the different solids up to 1000 °C (Fig. 8) resulted in an important increase in the relative intensities of the diffraction lines of the produced α -Al₂O₃. The comparison of the patterns of pure Al₂O₃ calcined at 900–1000 °C with those of different copper/aluminium mixed solids calcined at the same temperatures reveals that CuO stimulates the crystallization process of α -alumina (corundum), lowering the temperature of its formation from 1100 °C to about 900 °C. The exothermic peak at 975 °C observed in the DTA curve of CuAl-I solid might thus indicate the crystallization of α -Al₂O₃ according to



Enhancement of the crystallization process of α -Al₂O₃ has been found to take place in the presence of NiO and V₂O₅ [14]. However, the amount of V₂O₅ necessary to catalyse this phase transformation process is about 47 wt.% [14] instead of 16.3 wt.% in the case of cupric oxide. The mechanism(s)

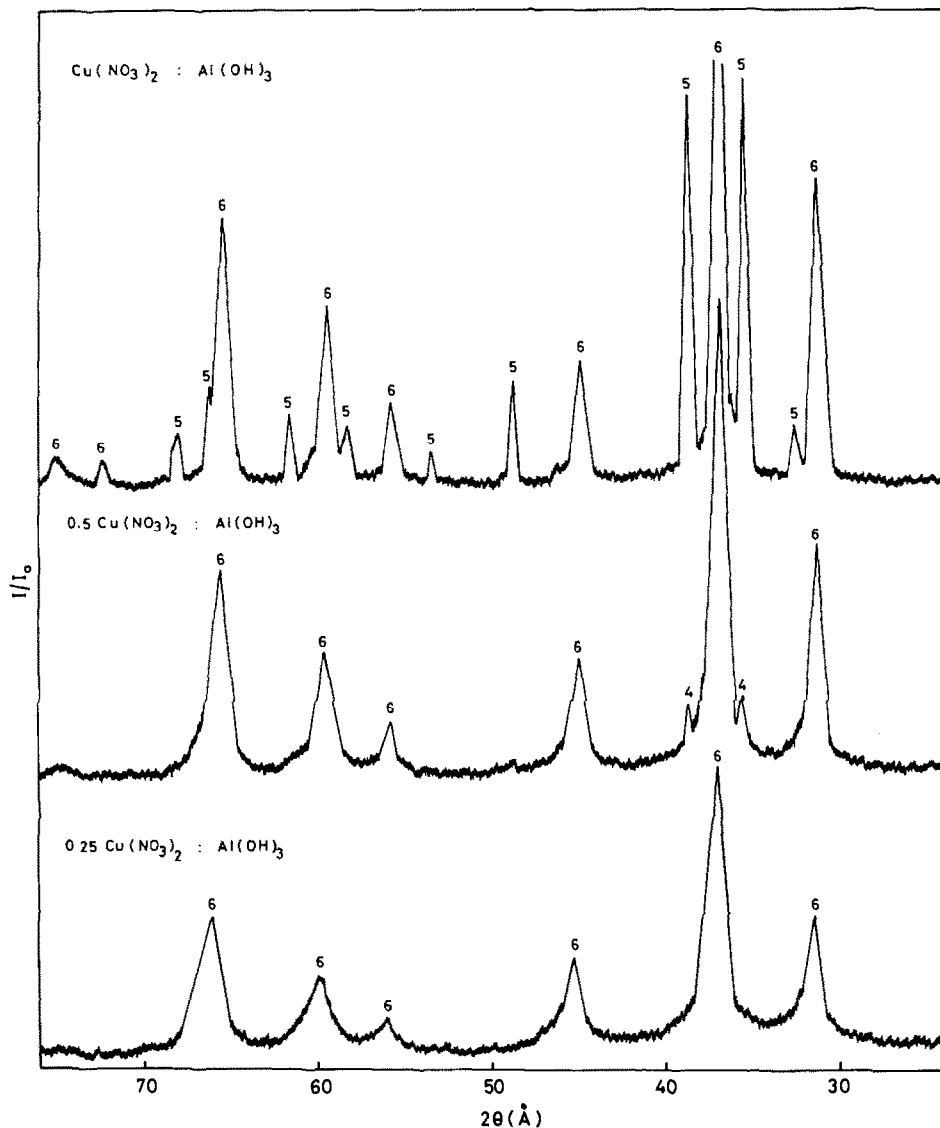


Fig. 6. X-ray diffractograms of various mixed oxide solids heated at 800°C : lines (4), $\alpha\text{-Al}_2\text{O}_3$; lines (5), CuO ; lines (6), CuAl_2O_4 .

of the $\alpha\text{-Al}_2\text{O}_3$ formation catalysed by certain foreign oxides (NiO , V_2O_5 and CuO) have not been discussed. It seems plausible to argue the formation of some kind of solid solution of these oxides in the alumina matrix which acts as nuclei for the crystallization process of the $\alpha\text{-Al}_2\text{O}_3$ phase.

Figure 9 shows the X-ray diffractograms of various mixed solids fired at 1100°C , and clearly indicates the thermal stability of the produced CuAl_2O_4 at this high temperature in the presence of excess alumina. The patterns of the mixed oxide solids containing an equimolar ratio of CuO and Al_2O_3

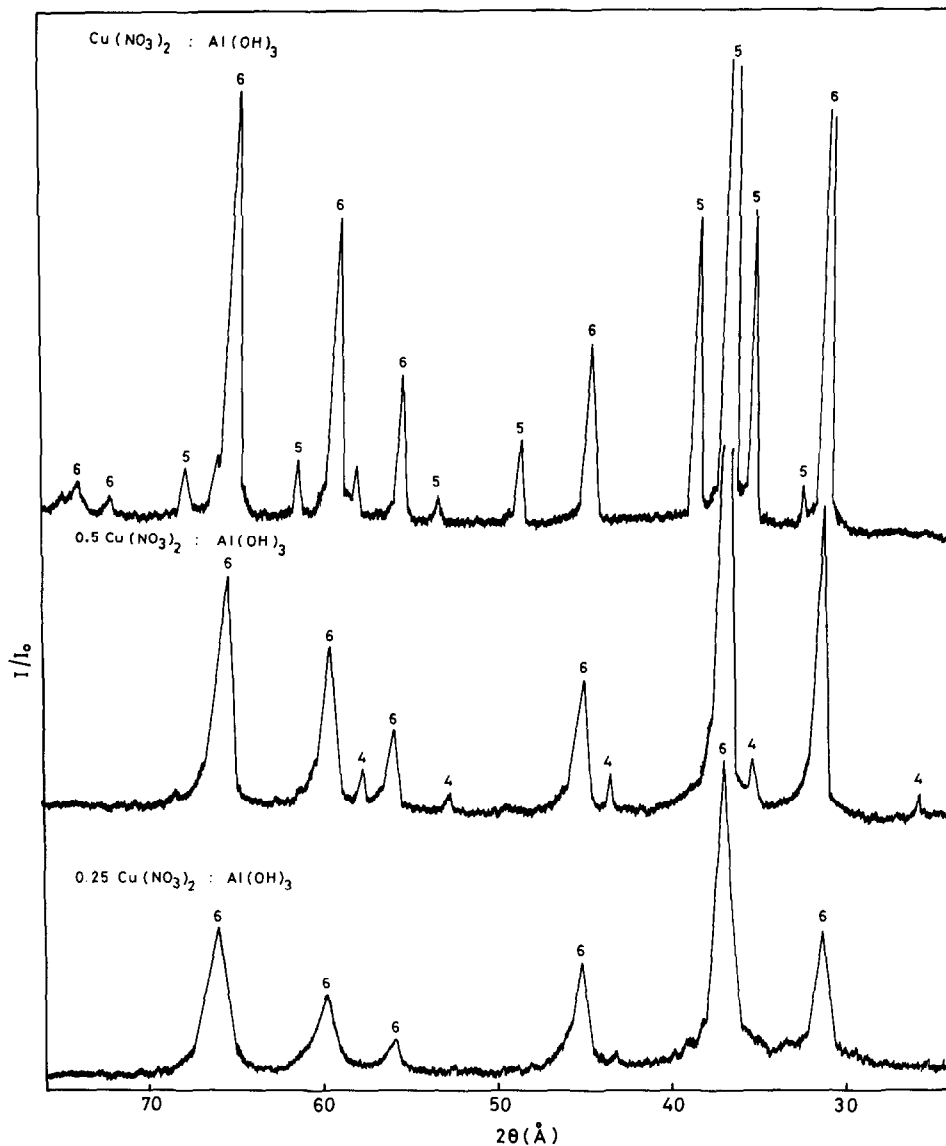
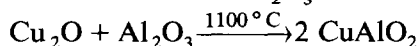


Fig. 7. X-ray diffractograms of different mixed solids precalcined at 900°C : lines (4), $\alpha\text{-Al}_2\text{O}_3$; lines (5), CuO ; lines (6), CuAl_2O_4 .

fired at 1100°C , consist of a mixture of highly crystalline CuAl_2O_4 and CuAlO_2 phases. The fact that copper aluminate remains thermally stable even when heated to 1100°C in the presence of excess Al_2O_3 might indicate that the alumina is stabilizing the aluminate phase. The CuAlO_2 present in the case of $\text{CuO} : \text{Al}_2\text{O}_3$ – 1100°C might result from the following reactions



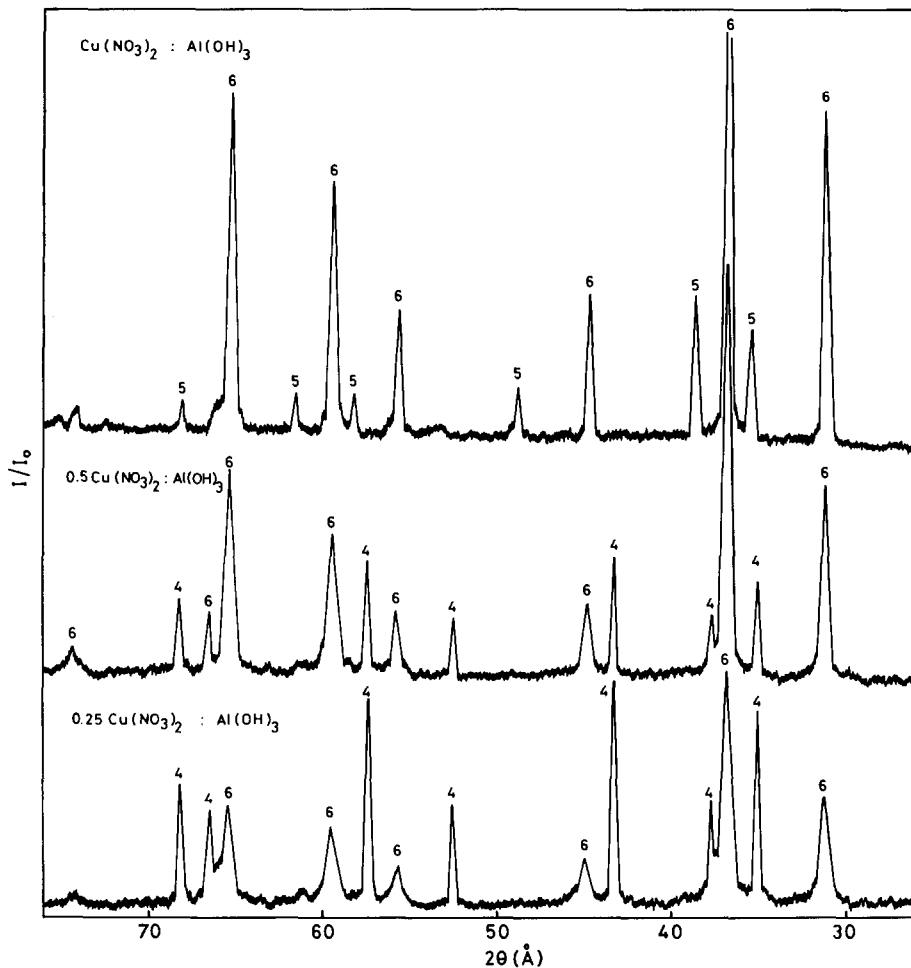


Fig. 8. X-ray diffractograms of various solids preheated at 1000 °C: lines (4), $\alpha\text{-Al}_2\text{O}_3$; lines (5), CuO; lines (6), CuAl_2O_4 .

It can be concluded that Al_2O_3 can be added in excess to suppress the previously mentioned reactions, i.e. to increase the thermal stability of the copper aluminate CuAl_2O_4 phase.

CONCLUSIONS

From the results obtained, we can conclude that: cupric oxide, produced from the thermal decomposition of cupric nitrate, interacts with the Al_2O_3 support to produce copper aluminate CuAl_2O_4 at temperatures starting from 650 °C; the copper aluminate produced remains thermally stable, even when heated to 1100 °C, in presence of excess Al_2O_3 and partly decomposes

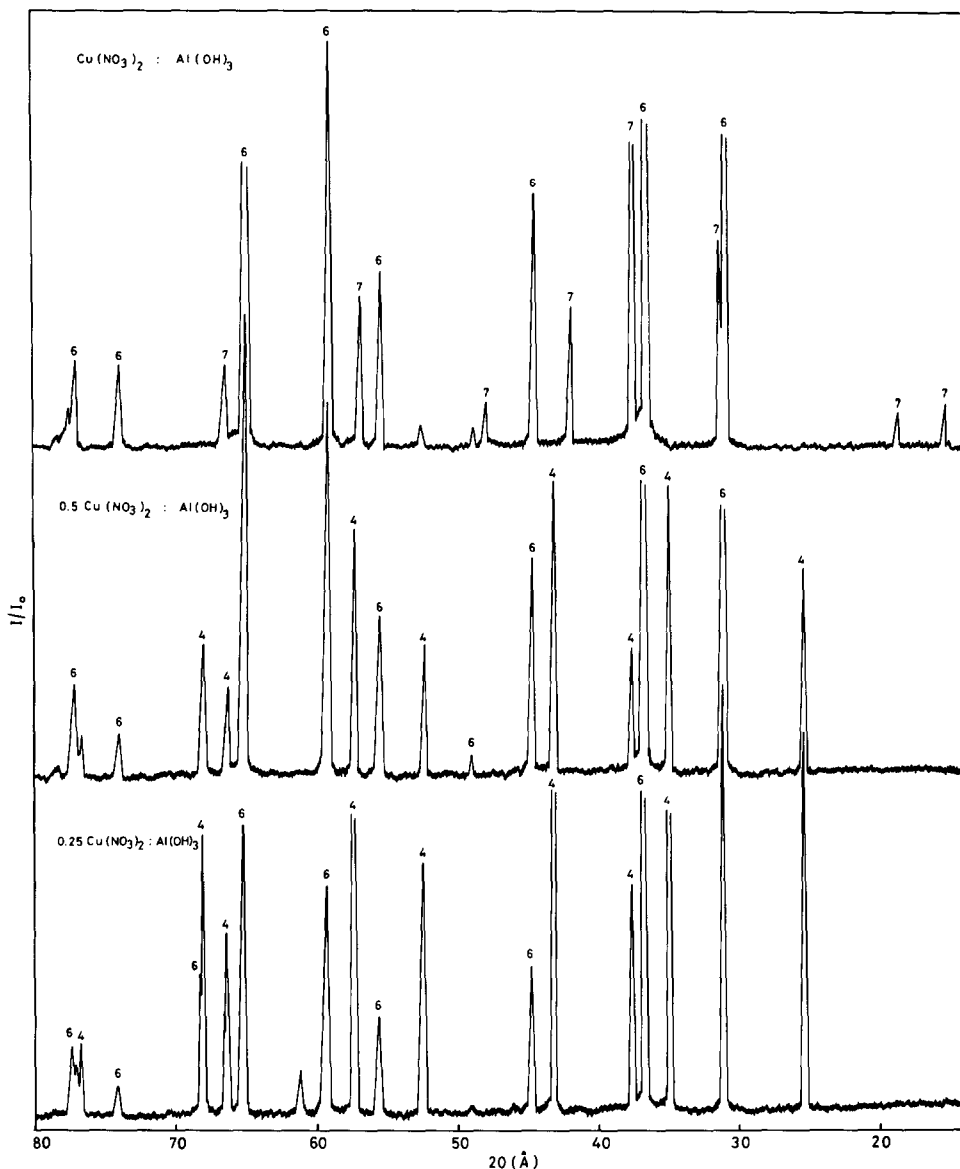


Fig. 9. X-ray diffractograms of different mixed solids fired at 1100°C: lines (4) $\alpha\text{-Al}_2\text{O}_3$; lines (6), CuAl_2O_4 ; lines (7), CuAlO_2 .

to CuAlO_2 in the case of mixed oxide solids containing an equimolar proportion of CuO and Al_2O_3 ; when heated in air at 900°C, the $\text{Al}(\text{OH})_3$ solid used consists of poorly crystalline $\gamma\text{-Al}_2\text{O}_3$ and at 1000°C it becomes a mixture of θ - and $\kappa\text{-Al}_2\text{O}_3$ that is moderately crystalline. The precalcination of these solids at 1100°C results in the formation of $\alpha\text{-Al}_2\text{O}_3$ together with the two other alumina phases; the presence of cupric oxide (16.3 wt.%)

stimulates or catalyses the formation of $\alpha\text{-Al}_2\text{O}_3$ at the lower temperature of around 900°C instead of 1100°C , in the case of pure aluminium oxide.

REFERENCES

- 1 M. Jayamani and C.N. Pillai, *J. Catal.*, 82 (2) (1983) 485.
- 2 V. Moravek and M. Kraus, *J. Catal.*, 87 (2) (1984) 452.
- 3 R. Miranda, D.J. Collins and B.H. Davis, *J. Catal.*, 88 (2) (1984) 542.
- 4 J.C. Luy and J.M. Parera, *Appl. Catal.*, 26 (1-2) (1986) 295.
- 5 P. Sidheswaran, N.J. Fafadia, V.A. Pol, S.U. Kulkarni, and R.S. Murthy, *Indian J. Technol.*, 25 (5) (1987) 247.
- 6 E.M. Ezzo, G.A. El-Shobaky and M.M. Selim, *Surf. Technol.*, 10 (1980) 47.
- 7 M.M. Selim, G.A. El-Shobaky and E.M. Ezzo, *Surf. Technol.*, 10 (1980) 75.
- 8 N.J. Rozlov, A.F. Yanchuk and L. Ya. Mostovaya, *React. Kinet. Catal. Lett.*, 19 (3-4) (1982) 337.
- 9 G.A. El-Shobaky and A.N. Al-Noaimi, *Surf. Technol.*, 26(3) (1985) 235.
- 10 G.A. El-Shobaky and A.N. Al-Noaimi, *Appl. Catal.*, 29 (1987) 235.
- 11 G.A. El-Shobaky, G.A. Fagal and A.M. Dessouki, *Radiat. Phys. Chem.*, 29 (1987) 39.
- 12 G.A. El-Shobaky, G.A. Fagal and T.M.H. Saber, *Bull. Soc. Chim. Fr.*, 4 (1987) 544; 4 (1987) 547; 4 (1987) 551.
- 13 G.A. El-Shobaky, Th. El-Nabarawy, N. Ghoneim and I.M. Morsi, *Surf. Technol.*, 19 (1983) 109.
- 14 G.A. El-Shobaky, K.A. El-Barawy and F.H.A. Abdalla, *Thermochim. Acta*, 96 (1986) 181.
- 15 D.H. Anotonian, K. Jersy and J. Kalik, *Zesz. Nauk Politech. Slask. Chem.*, 53 (1970) 107.
- 16 J. Zemlica and C. Barta, *Krist. Technol.*, 7 (1972) 965.
- 17 A. Lycourghiotis, D. Vattis, P. Aroni and N. Katsanos, *Acta. Chim. Acad. Sci. Hung.*, 109 (1982) 261.
- 18 A. Lycourghiotis, V. Dimitris and A. Nicholas; *Z. Phys. Chem.*, 125 (1981) 95.