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MUTUAL SOLID–SOLID INTERACTION BETWEEN CuO AND SODIUM OXIDE-DOPED ALUMINA

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ABSTRACT

The solid–solid interactions between CuO and Al_2O_3 doped with Na_2O were investigated using DTA and XRD techniques. The content of copper oxide was fixed at 16.3 wt.% and that of sodium oxide was varied between 1.87 and 7.49 wt.%. The different solids were preheated in air at 500–1000 ° C for 8 h.

The results obtained reveal that the pure mixed solids were amorphous at 500 ° C. Doping with Na_2O at this temperature resulted in the appearance of CuO diffraction lines having intensities that increase with the amount of the oxide dope added. Thermal treatment of the pure mixed solid samples at 800 ° C brought about a solid–solid interaction between CuO and Al_2O_3 producing $CuAl_2O_4$. The excess alumina remained as an amorphous phase. The presence of sodium oxide was found to inhibit copper aluminate formation to an extent proportional to the amount of Na_2O present. This effect was attributed to the formation of a layer of sodium aluminate that covers the surfaces of the Al_2O_3 grains and hinders the thermal diffusion of Cu^{2+} ions into the Al_2O_3 matrix. The inhibition effect of Na_2O toward $CuAl_2O_4$ formation was also observed for the doped solids heated at 900 and 1000 ° C.

At 1100 ° C Al_2O_3 was found to exist as a mixture of θ-, κ- and α-aluminas and the transformation of these phases into α-Al_2O_3 required heating at >1100 ° C. However, the presence of CuO was found to stimulate the crystallization of α-alumina at temperatures >900 ° C, while the presence of Na_2O prevented completely the formation of α-Al_2O_3 at 900 ° C and also decreased the amount produced at 1000 ° C. The addition of 7.49% Na_2O prevented completely the appearance of α-alumina even after heating at 1000 ° C, and led to the formation of β-alumina, $NaAl_2O_8$, at between 900 and 1000 ° C.

INTRODUCTION

The physicochemical and catalytic properties of different transition metal oxides supported on Al_2O_3 are mainly dependent on the method of preparation of the raw materials involved in their preparation, calcination conditions, extent of loading, subjection to ionizing radiation and doping with certain foreign cations [1–15].

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Solids prepared by coprecipitation are homogeneous in structure, highly dispersed and have large specific surface areas (some hundreds of $m^2\ g^{-1}$) [4,11,12,18]. However, they exhibit catalytic activities (for CO oxidation) smaller than those measured for solids prepared by impregnation processes [11,12]. The percentage loading of a supported metal oxide of $< 5\%$ leads to the formation of a highly dispersed metal oxide phase, even at about 600 °C [10,15,16]. The increase in the extent of loading above this limit results in the formation of large well-developed crystallites of the metal oxide. Furthermore, solid–solid interactions between metal oxides and the Al_2O_3 support occur at temperatures above 500 °C yielding the corresponding aluminate compound [14–16]. Gamma-irradiation has been reported to greatly affect the physicochemical and catalytic properties of different supported solids [9,13]. The addition of small amounts of certain foreign cations such as Li^+, Na^+, K^+ and Zn^{2+} has been found to exert significant changes on solid–solid interactions between the metal oxides and Al_2O_3 and on the degree of dispersion of the catalytically active constituents on the support surface [14,16,17].

The present work is devoted to studying the effect of Na_2O-doping of the Al_2O_3 support on mutual solid–solid interactions between CuO and Al_2O_3. The techniques employed were DTA and XRD.

EXPERIMENTAL DETAILS

Materials

Pure aluminium hydroxide of analytical grade was supplied by the Prolabo company. A given mass of finely-powdered $Al(OH)_3$ was impregnated with a solution containing different proportions of sodium nitrate, dried at 110 °C. and then calcined in air at 500 °C for 6 h. The amounts of sodium, expressed in wt.% Na_2O, were 1.87, 3.74 and 7.49. The sodium-impregnated Al_2O_3 specimens were then treated with a solution containing a known amount of $Cu(NO_3)_2 \cdot 3H_2O$, dried at 110 °C and calcined in air at different temperatures between 500 and 1000 °C. The time of heating was fixed at 8 h. The extent of copper, expressed in wt.% CuO, was fixed at 16.3.

Techniques

DTA analyses of various solids were carried out using a Netzsch–Gerätebau simultaneous thermal analysis apparatus (STA 409, type 6.223). The rate of heating was kept at 10 °C min^{-1}. A 50 mg sample of each solid specimen was analysed in each case.

X-ray investigations of the calcined specimens were performed with a Philips diffractometer (type PW 1390). The patterns were obtained with nickel-filtered copper radiation ($\lambda = 1.5405$ Å) at 36 kV and 16 mA with a scanning speed of 1° in $2\theta\ min^{-1}$.

RESULTS AND DISCUSSION

Thermal behaviour of pure and doped mixed solids

Figure 1 shows the DTA curves of pure and doped solids. These mixed solids exhibit three endothermic peaks: the first two are sharp and strong with maxima located at 250 and 300 °C; the third peak is weak and broad with its maximum at about 650 °C. An additional exothermic peak at 975 °C was only observed in the DTA curve of the pure mixed solid. The peaks at 250 and 300 °C correspond to the thermal decomposition of copper nitrate and aluminium hydroxide. The peak at 650 °C may indicate a solid–solid interaction between the copper thus produced and aluminium oxides, and the exothermic peak at 975 °C may characterize a phase transformation. The identification of these processes was performed using XRD measurements (see below).

XRD of pure and doped mixed solids

Preliminary experiments showed that the aluminium hydroxide calcined in air at temperatures up to 700 °C was an amorphous solid. The poorly

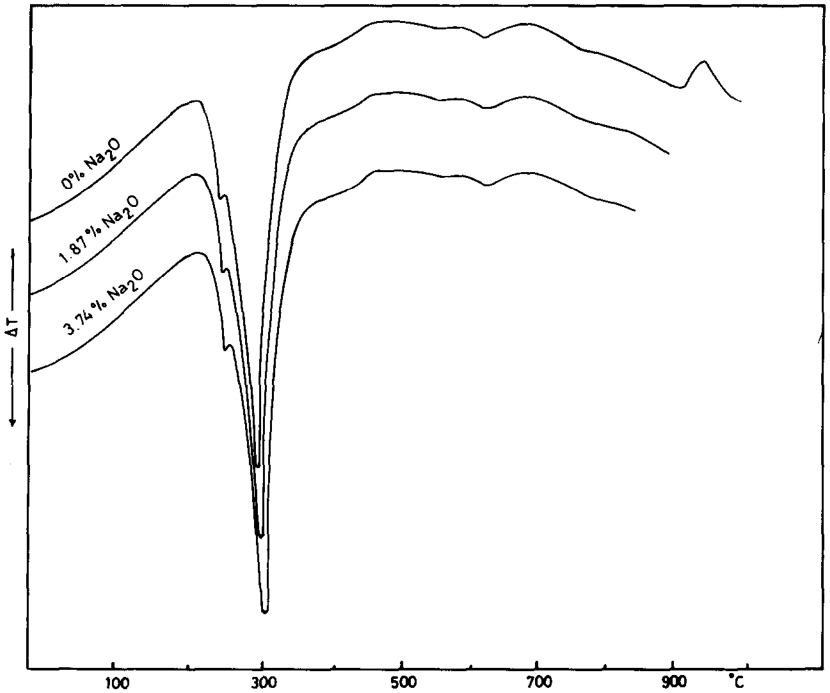

Fig. 1. DTA curves of pure and Na_2O-doped mixed $CuO–Al_2O_3$ solids.

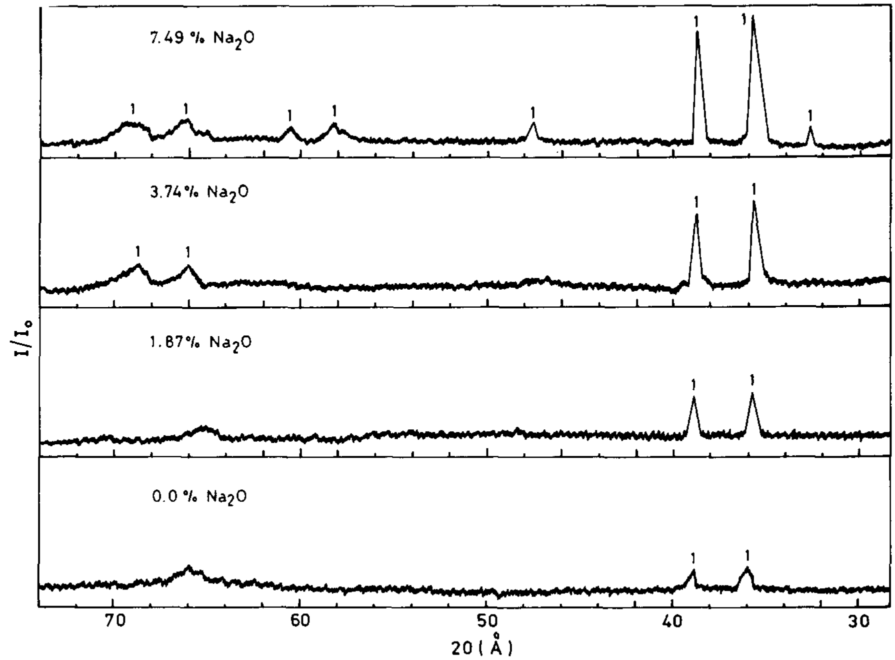

Fig. 2. X-ray diffractograms of pure and Na_2O-doped mixed $CuO-Al_2O_3$ solids heated at 500 ° C. CuO peaks.

crystalline γ-Al_2O_3 was formed by heating the parent hydroxide at 800 ° C, and at 1100 ° C the products were a mixture of κ-, θ- and α-alumina phases. The complete transformation into α-Al_2O_3 required a prolonged heating at elevated temperature > 1200 ° C [18]. Figure 2 shows X-ray diffractograms of pure and different Na_2O-doped aluminas impregnated with cupric nitrate solution and calcined in air at 500 ° C. This figure indicates the amorphous nature of the pure mixed solids. The characteristic diffraction lines of the CuO phase were found in the patterns of the doped mixed solids. The degree of crystallinity of cupric oxide was increased by increasing the extent of Na_2O added. These results have been discussed in our recent investigation [19] and were attributed to occupation by Na^+ ions in tetrahedral and octahedral sites of the Al_2O_3 surface thus decreasing effectively the monolayer dispersion capacity of Al_2O_3 for the CuO phase [15]. It has also been concluded that sodium doping of Al_2O_3 enhances the crystallization process of CuO solid. The rise in the precalcination temperature of the various solids investigated above 500 ° C may result in solid–solid interactions between the different constituents of the employed mixed solid specimens.

Figure 3 shows the X-ray diffractograms of pure and doped solids preheated at 800 ° C. It can be observed from Fig. 3 that the pure mixed solids consist of copper aluminate of medium crystallinity. It can also be seen that Na_2O-doping of the Al_2O_3 support decreases the amount of

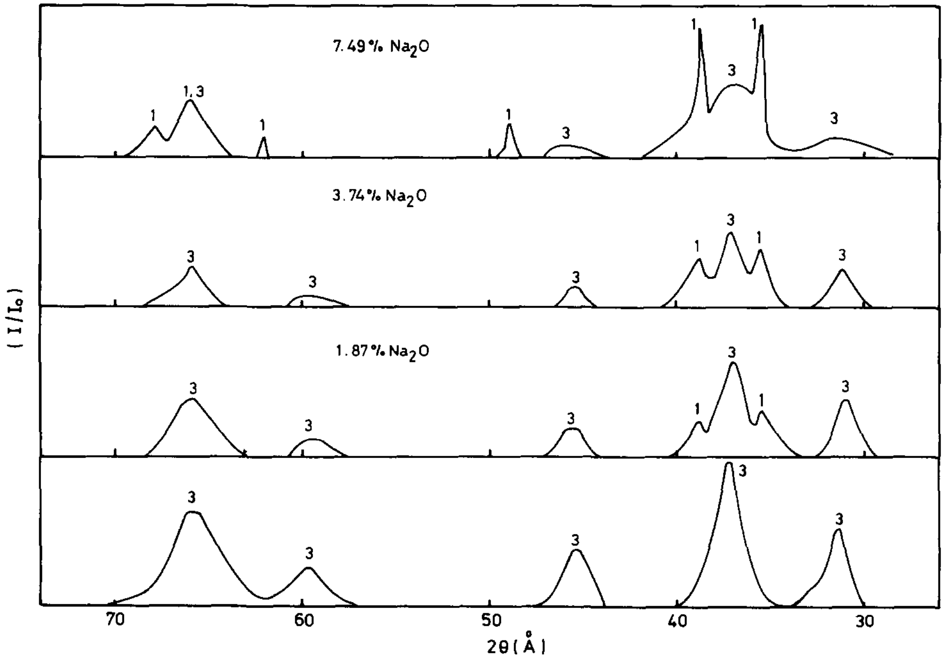

Fig. 3. X-ray diffractograms of pure and Na_2O-doped mixed $CuO-Al_2O_3$ solids heated at 800 °C. Peaks: (1) CuO, (2) α-Al_2O_3, (3) $CuAl_2O_4$.

$CuAl_2O_4$ produced to an extent proportional to the amount of oxide added. This conclusion is reached by comparing the areas of different diffraction peaks of copper aluminate. The mixed solid sample treated with 7.49 wt.% Na_2O and preheated at 800 °C was constituted of highly crystalline non-reacting CuO phase together with a small amount of $CuAl_2O_4$. The complete prevention of copper aluminate formation at 800 °C thus requires doping with Na_2O in amounts greater than 7.49%. The inhibition effect of sodium oxide on the formation of $CuAl_2O_4$ may be caused by the formation of sodium aluminate during the thermal treatment of $NaNO_3$-treated Al_2O_3 at 500 °C. The sodium aluminate so produced may cover the surfaces of the Al_2O_3 grains, thus hindering the thermal diffusion of Cu^{2+} ions into Al_2O_3 matrix where interaction would otherwise occur to yield $CuAl_2O_4$. The sodium aluminate acts as an energy barrier which must be overcome, so the effective formation of copper aluminate requires thermal treatment of the doped solids at temperature above 800 °C.

Figure 4 presents the X-ray diffractograms of pure and doped mixed solids preheated at 900 °C. The diffraction lines of both $CuAl_2O_4$ and α-Al_2O_3 (corrundum) of reasonable crystallinity were only detected in the patterns of pure solids, these results clearly indicate that CuO stimulates the formation of the α-phase and lowers the temperature of its formation from about 1100 °C to 900 °C. However, addition of the smallest amount of

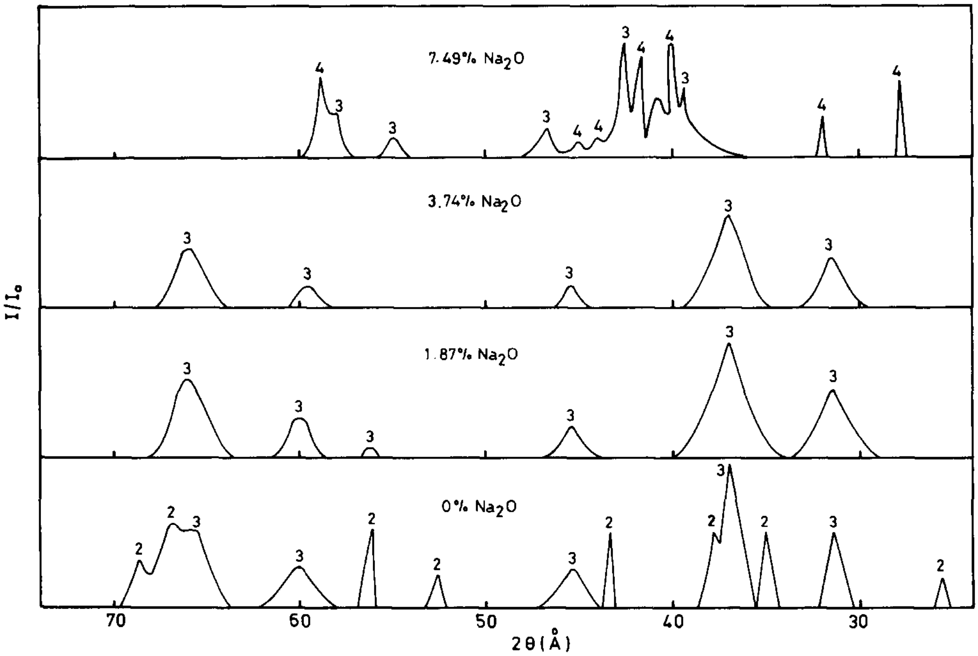

Fig. 4. X-ray diffractograms of pure and Na_2O-doped mixed Al_2O_3–CuO solids heated at 900 °C. Peaks: (1) CuO, (2) α-Al_2O_3, (3) $CuAl_2O_4$, (4) $NaAl_2O_8$.

Na_2O (1.87%) prevented completely the crystallization of aluminium oxide to α-Al_2O_3. It can be seen from Fig. 4 that Na_2O also inhibits the formation of $CuAl_2O_4$ at 900 °C to an extent proportional to the amount of sodium added. The presence of 7.49 wt.% Na_2O, beside its effective role in decreasing the amount of copper aluminate formed, resulted in the formation of sodium aluminate, $NaAl_2O_8$, of reasonable crystallinity. The formation of sodium aluminate as a result of low-level doping with Na_2O and at tempertures below 900 °C could not be ruled out. The inhibition effect of Na_2O in $CuAl_2O_4$ formation can thus be understood on the basis of formation of sodium aluminate which covers the surfaces of grains of Al_2O_3 and opposes the thermal migration of copper ions into the sodium-doped alumina. Also, the role of sodium oxide in preventing the formation of α-corrundum at 900 °C can be attributed to the coating of the doped alumina sample by $NaAl_2O_8$ which has the structure of β-alumina [20] and thus hinders the transformation of free Al_2O_3 (not contributing in the formation of sodium aluminate) to α-corrundum. The augmentation of the precalcination temperture of various doped solids above 900 °C could result in the crystallization of α-alumina.

Figure 5 shows the X-ray diffractograms of pure and doped solids pre-heated at 1000 °C. It can be seen from this figure that the pure solids consist of a mixture of very highly crystallized copper aluminate and

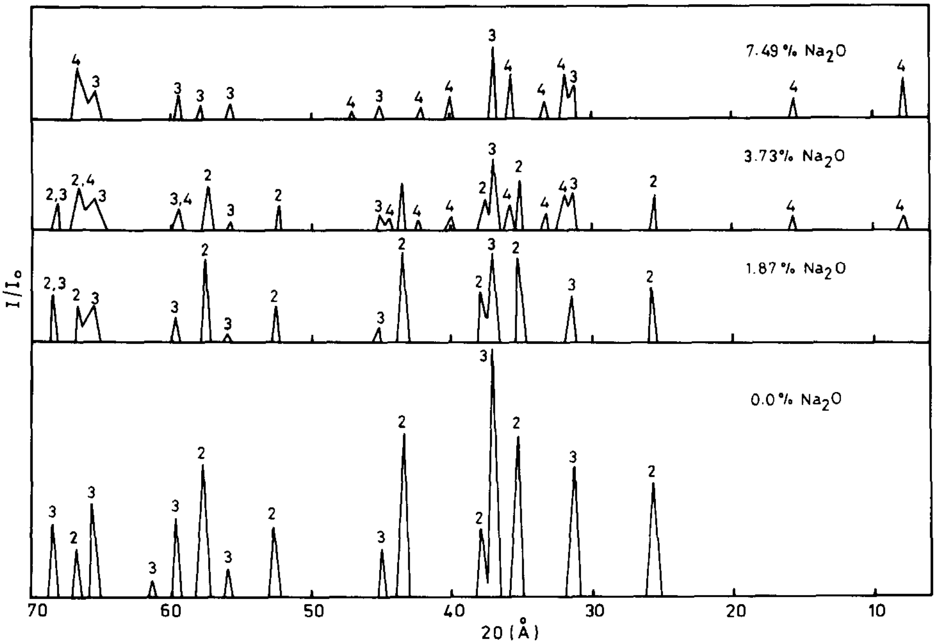

Fig. 5. X-ray diffractograms of pure and Na_2O-doped mixed $CuO-Al_2O_3$ solids heated at 1000 °C. Peaks: (1) CuO, (2) α-Al_2O_3, (3) $CuAl_2O_4$, (4) $NaAl_2O_8$.

α-alumina (corrundum). These results point again to the role of CuO phase (16.3 wt.%) in catalyzing the crystallization process of Al_2O_3 into α-alumina at 1000 °C.

Figure 5 shows also that the addition of small amounts of Na_2O (1.87%) to the Al_2O_3 samples brought about a considerable decrease in the relative intensities of all diffraction lines of both copper aluminate and α-alumina. Increasing the amount of sodium oxide to 3.74 wt.% resulted in a further decrease in the amounts of produced copper aluminate and α-alumina and also led to the formation of sodium aluminate which has the β-alumina structure. When the amount of sodium oxide added reached 7.49 wt.% all the diffraction lines of α-Al_2O_3 disappeared from the patterns of the mixed solids preheated at 1000 °C and the relative intensities of the diffraction lines of $NaAl_2O_8$ were effectively increased. This indicates that most of Na_2O added to the alumina specimens contributed to the formation of the detected sodium aluminate phase. In other words, the catalyzing effect of CuO in the formation of α-corrundum at 1000 °C could be entirely eliminated by the addition of 7.49 wt.% Na_2O.

The fact that the amount of Na_2O necessary to prevent the crystallization of α-Al_2O_3 by heating CuO/Al_2O_3 solids at 900 °C (cf. Fig. 4) was only 1.87% might indicate that the sodium aluminate formed at this temperature completely covered the surface of Al_2O_3 grains hindering its transformation into α-corrundum. The inhibition effect of sodium oxide in the crystallization of aluminium oxide to α-corrundum at 900–1000 °C can thus be understood. Similarly, the role of Na_2O in opposing the solid–solid interaction between CuO and Al_2O_3 may be attributed mainly to the spreading of sodium aluminate on the surfaces of Al_2O_3 grains thus making the thermal migration of copper ions through the interior of these grains difficult. However, one cannot overlook the role of sodium-doping of CuO which might be followed by a slight overall increase in its oxidation number [21]. The copper ions with an induced higher oxidation state may not contribute in the formation of $CuAl_2O_4$ spinel. In fact, copper aluminate is normally produced by interaction between divalent copper ions and Al_2O_3. The retardation effect of sodium-doping in $CuAl_2O_4$ formation according to the last mechanism is of minor importance, simply because the amount of sodium ions that can be dissolved in CuO lattice is very small owing to their relatively large ionic radius (0.95 Å) as compared to that of Cu^{2+} ions (0.78 Å) [4] and of the contribution of most of sodium ions present in the formation of sodium aluminate compound.

CONCLUSIONS

The main conclusions that can be formulated from the results obtained can be summarized as follows:

(1) Sodium oxide-doping of CuO/Al_2O_3 solids enhances the crystallization process of the CuO phase at 500 °C owing to the location of Na^+ ions in octahedral and tetrahedral sites of Al_2O_3 support. This process is normally accompanied by an important decrease in the dispersion capacity of Al_2O_3 toward CuO.

(2) The doping process greatly inhibits the formation of both copper aluminate and α-Al_2O_3 at 900–1000 °C, to an extent proportional to the amount of sodium oxide added.

(3) Na_2O added to different mixed solids interacts with Al_2O_3 at 900 °C to yield $NaAl_2O_8$ which has a β-alumina structure. The sodium aluminate so produced then covers the surfaces of the Al_2O_3 grains, hinders its crystallization to α-corrundum and opposes the thermal diffusion of Cu^{2+} ions into the interior of the solid Al_2O_3 matrix.

(4) The role of Na_2O-doping in inhibiting the formation of $CuAl_2O_4$ may also be attributed to the possible dissolution of a small proportion of the Na^+ ion into the CuO matrix, leading to an increase in the oxidation number of some of the copper ions. These ions may not then participate directly in the formation copper aluminate spinel.

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