Thermochimica Acta, 150 (1989) 111–120
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EFFECTS OF Li_2O DOPING ON SOLID–SOLID INTERACTIONS IN THE $CuO–Al_2O_3$ SYSTEM

G.A.EL-SHOBAKY, TH. EL-NABARAWY and G.A. FAGAL

National Research Centre, Dokki, Cairo (Egypt)

(Received 25 January 1989)

ABSTRACT

The results obtained reveal that pure $CuO–Al_2O_3$ solids, containing 16.3 wt.% copper oxide and preheated in air at 500 °C, are amorphous and change to crystalline phases on doping with Li_2O (0.3–3.57 wt.% Li_2O). The diffraction lines of the CuO phase are only detected in the XRD patterns of the doped solids precalcined at 500 °C. The degree of crystallinity of this phase increases on increasing the amount of Li_2O added. Solid–solid interaction between pure or doped alumina and CuO occurs at 800 °C to yield a massive $CuAl_2O_4$ phase with moderate crystallinity, whereas the excess alumina remains as an amorphous phase. However, in the doped solids increasing amounts of unreacted crystalline CuO phase are found in the patterns, indicating that the doping process opposes the solid–solid interaction between CuO and Al_2O_3. These results can be attributed to the production of lithium aluminate and to the formation of an $Li_2O–CuO$ solid solution. The aluminate compound produced 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 portion of the CuO phase that dissolves Li_2O cannot contribute easily to the interaction with Al_2O_3 to give copper aluminate. Copper oxide stimulates the crystallization of alumina into α-Al_2O_3 (corundum) at temperatures starting from 900 °C, whereas lithium oxide doping hinders this crystallization process to an extent proportional to the amount of dopant oxide added. The addition of 3.57 wt.% Li_2O is sufficient to suppress completely the crystallization of α-Al_2O_3 or any other crystalline form of the doped alumina even when firing at 1000 °C.

INTRODUCTION

The catalytic activities of transition metal oxides are significantly increased by loading on an alumina support [1–10]. This increase is attributed to an effective increase in the degree of dispersion of the loaded oxides. However, chemical interactions between these oxides and Al_2O_3 take place at temperatures starting from 500 °C [11–16]. It has been reported that two types of reactions may occur concurrently, according to the nature of the transition metal oxide and to the conditions of preparation: one leads to the formation of a "surface" metal aluminate spinel and the other to the

0040-6031/89/$03.50

segregation of a stable metal oxide [11–16]. The addition of small amounts of certain foreign cations such as Li^+, Na^+, Zn^{2+}, Ca^{2+}, Sr^{2+}, Ga^{3+} and Ge^{4+} to the aluminas has been found to influence the chemical interactions between the loaded oxides and their support [17–21]. This influence may be accompanied by significant changes in the catalytic activities of the doped supported catalysts [5,7,16].

The effect of Na_2O doping of $CuO–Al_2O_3$ solids on the chemical interactions between their constituents was the object of a recent investigation [22]. Na_2O doping inhibits the solid–solid interactions between CuO and Al_2O_3 which yield $CuAl_2O_4$ at temperatures between 800 and 1000 °C and also suppresses the crystallization of α-alumina.

This work was conducted to study the effect of lithium oxide doping of an Al_2O_3 support on the solid–solid interactions between CuO and Al_2O_3. The techniques employed were differential thermal analysis (DTA) and X-ray diffraction (XRD).

EXPERIMENTAL

Materials

The aluminium hydroxide was of analytical grade and was supplied by the Prolabo company. A given mass of a finely powdered $Al(OH)_3$ sample was impregnated with a solution containing different proportions of lithium nitrate. This was then dried at 110 °C and calcined in air at 500 °C for 6 h. The amounts of lithium, expressed as Li_2O, were 0.30, 0.89, 1.79 and 3.57 wt.%. The lithium-modified 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 heated in air at temperatures in the range 500–1000 °C. The time of heating was fixed at 6 h. The amount of copper, expressed as CuO, was fixed at 16.3 wt.%.

Techniques

Differential thermal analysis of various solids was performed using a Netzsch–Gerätebau simultaneous thermal analysis apparatus (STA 409, type 6.223). The rate of heating was maintained at 10 °C min^{-1}. A 50 mg sample of each solid specimen was employed in each case.

X-ray investigation of the calcined solids was carried out using 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 2θ 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 solids exhibit three endothermic peaks. The first two are sharp and strong with maxima at 250 and 300 °C. The third peak is weak and broad with a maximum at about 650 °C. An additional exothermic peak at 975 °C is observed in the DTA curve of the pure mixed solid specimen. The peaks at 250 and 300 °C indicate the thermal decomposition of copper nitrate and aluminium hydroxide respectively. The peak at 650 °C may correspond to solid–solid interaction between the copper and aluminium oxides produced. The exothermic peak at 975 °C may correspond to a phase transformation process. The identification of these thermal processes was carried out using XRD measurements (see below).

X-ray diffraction of the thermal products of pure and doped $CuO–Al_2O_3$ solids

It has been reported previously [22] that $Al(OH)_3$ preheated in air at 500–700 °C is an amorphous solid and changes to a mixture of crystalline κ-, θ- and α-Al_2O_3 phases on heating at 1100 °C. The complete transformation into α-alumina requires prolonged heating at $>$ 1200 °C [23].

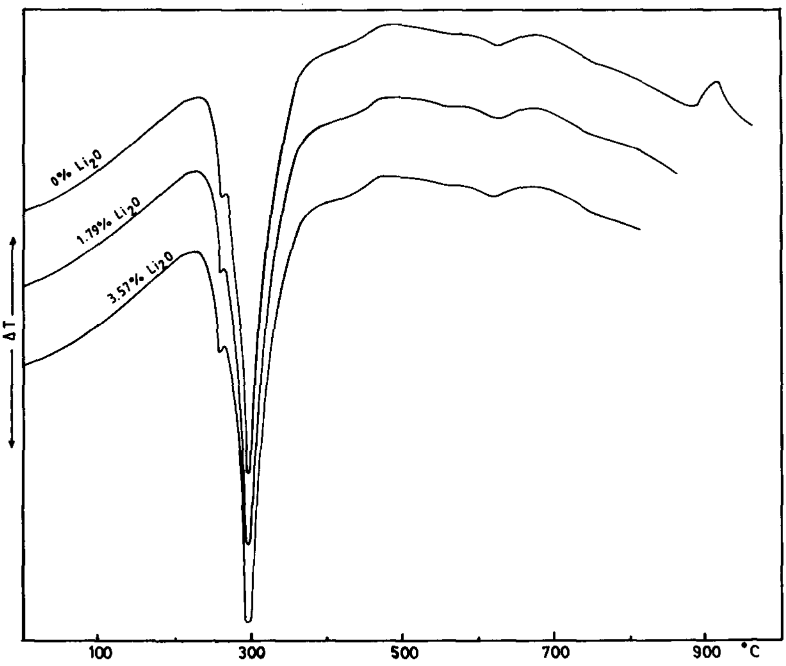

Fig. 1. DTA curves of pure and doped $CuO–Al_2O_3$ solids.

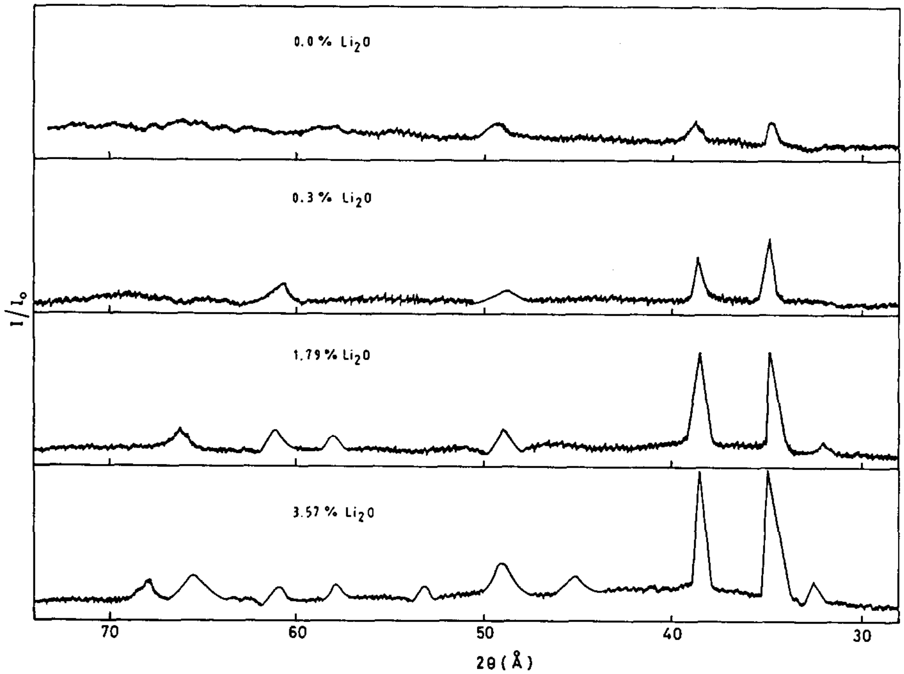

Fig. 2. X-ray diffractograms of pure and doped CuO–Al_2O_3 solids.

Figure 2 shows X-ray diffractograms of pure and doped aluminas impregnated with copper nitrate and calcined at 500 °C. It can be seen from this figure that the pure mixed solid sample is amorphous in nature. The diffraction lines of the CuO phase can be seen in the patterns of the doped solids. The degree of crystallinity of the detected CuO phase increases as a function of the amount of Li_2O added. The observed effect of Li_2O is similar to that reported for Na_2O [22]. However, lithium oxide doping is more efficient in increasing the crystallinity of the CuO phase. These findings can be attributed to the location of the alkali metal ions in the tetrahedral and octahedral sites of the Al_2O_3 surface, thus effectively decreasing the monolayer dispersion capacity (MLDC) of the Al_2O_3 support for the CuO phase [24]. The MLDC of a support is defined as its capacity to keep the loaded phase in an amorphous state. This is probably due to the formation of a two-dimensional metal-support compound or to the existence of the loaded phase as cations spread on the support surface [24–27]. This capacity is generally expressed as the weight per cent of the loaded oxide per 100 m^2 of the support. The lithium ions of the dopant agent progressively occupy Al_2O_3 sites, thus suppressing the formation of a two-dimensional CuO–Al_2O_3 compound or opposing the presence of Cu^{2+} on the surface of the alumina support. The effect of foreign cations in modifying the dispersion capacity of the Al_2O_3 support towards loaded copper oxide or any other oxide has not yet been investigated to our knowledge.

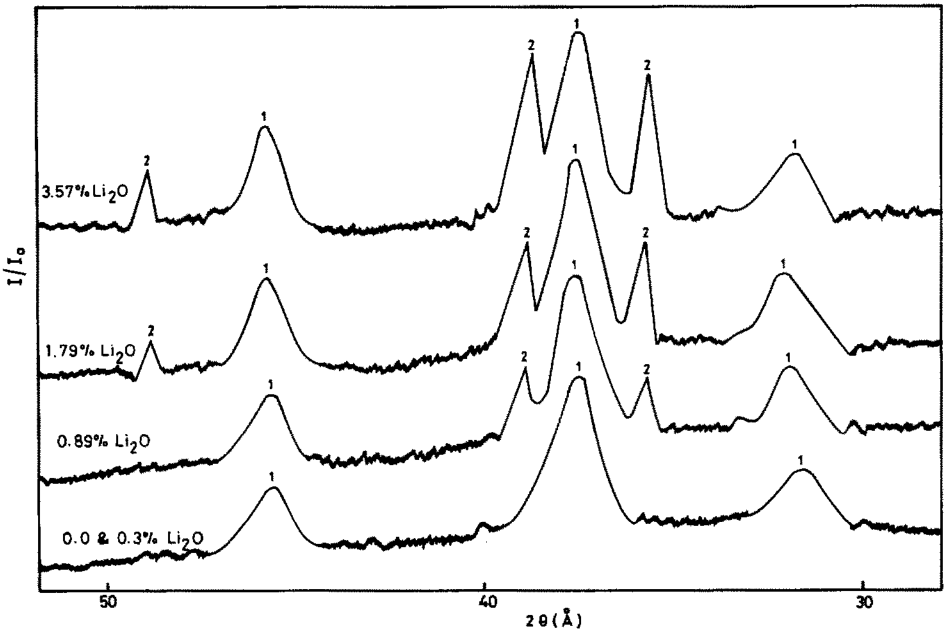

Fig. 3. XRD patterns of pure and doped solids precalcined at 800 °C: 1, $CuAl_2O_4$ phase; 2, CuO phase.

An increase in the preheating temperature of the pure and doped $CuO-Al_2O_3$ solids above 500 °C can lead to solid–solid interaction between the different constituents of these solids. Figure 3 shows X-ray diffractograms of pure and doped solid samples precalcined at 800 °C. This figure shows that the pure $CuO-Al_2O_3$ solid consists entirely of the moderately crystalline $CuAl_2O_4$ phase, whereas the excess alumina in this sample exists as an amorphous phase. This clearly indicates that CuO, in the pure mixed solid specimen, interacts completely with its alumina support to yield the copper aluminate compound. It can also be seen from Fig. 3 that the diffraction lines of the CuO and $CuAl_2O_4$ phases are detected in the patterns of the doped solids and the intensities of the lines of the CuO phase increase as a function of the amount of Li_2O present. It can thus be concluded that Li_2O doping of the alumina support hinders its interaction with copper oxide. These results can be attributed to the formation of an Li_2O-CuO solid solution [28,29] and lithium aluminate [30]. Indeed it has been reported that lithium oxide interacts with Al_2O_3 at about 600 °C to give $LiAl_5O_8$ [30]. This compound covers the surfaces of the Al_2O_3 grains and thus hinders the thermal diffusion of Cu^{2+} ions into the Al_2O_3 matrix. Copper oxide can dissolve Li_2O and this process is normally accompanied by an increase in the oxidation state of the doped CuO solid. The dissolution of Li_2O in the CuO lattice can be simplified by adopting Kröger's notions [31] as follows

$$Li_2O + \tfrac{1}{2}O_2(g) \rightarrow Li^+(Cu^{2+}) + 2(+)$$

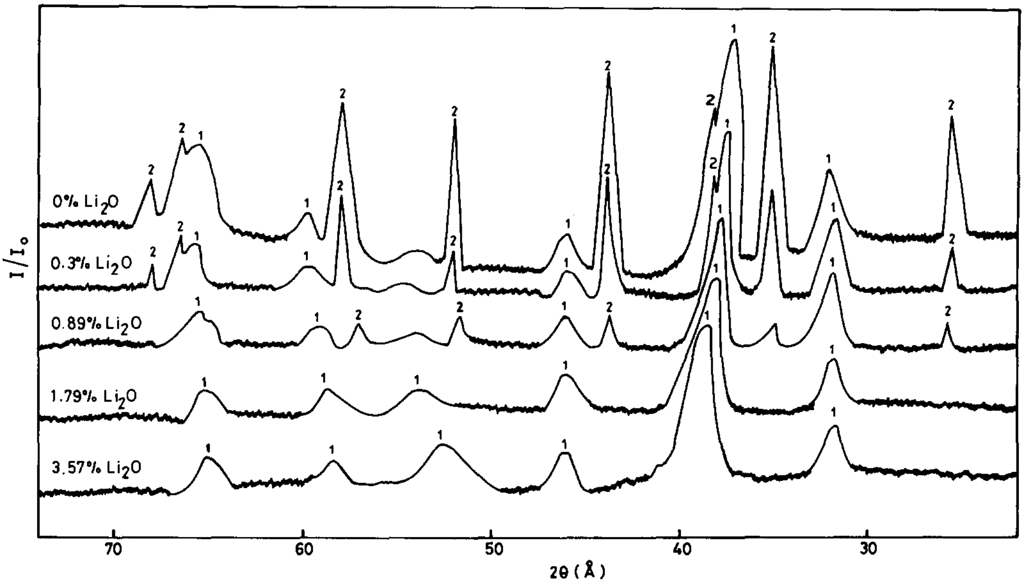

Fig. 4. XRD patterns of pure and doped solids preheated at 900 ° C: 1, $CuAl_2O_4$ phase; 2, α-Al_2O_3 (corundum) phase.

$Li^+(Cu^{2+})$ represents a lithium ion located in the position of the host cation of the CuO solid and (+) is a created positive charge responsible for the increase in the oxidation state of the doped copper oxide. It is known that the formation of $CuAl_2O_4$ spinel occurs between CuO in the divalent state and Al_2O_3 in the trivalent state. Therefore the increase in the oxidation state of copper oxide due to doping can lead to the formation of copper ions which are not capable of interacting with Al_2O_3 to yield $CuAl_2O_4$. The lithium aluminate produced which covers the surfaces of the Al_2O_3 grains and the Li_2O–CuO solid solution formed act as energy barriers for the formation of copper aluminate. The barrier created by lithium aluminate ($LiAl_5O_8$) may be overcome by heating the doped solids at temperatures above 800 ° C. At these temperatures the copper ions Cu^{2+} can more easily diffuse through the lithium aluminate to reach Al_2O_3 and interact with it.

Figure 4 shows the X-ray diffractograms of pure and doped solids precalcined in air at 900 ° C. It can be seen from this figure that the pure solid specimen and those doped with 0.30 or 0.89 wt.% Li_2O consist of well-crystallized $CuAl_2O_4$ and α-alumina (corundum). The other doped solid specimens consist of well-crystallized copper aluminate only. The relative intensities of the diffraction lines of α-alumina in the doped solids decrease on increasing the amount of Li_2O added (cf. Fig. 4). These results clearly indicate that lithium oxide doping leads to a decrease in the crystallization process of α-Al_2O_3 at 900 ° C to an extent proportional to the amount of dopant agent present. The role of Li_2O doping in suppressing the

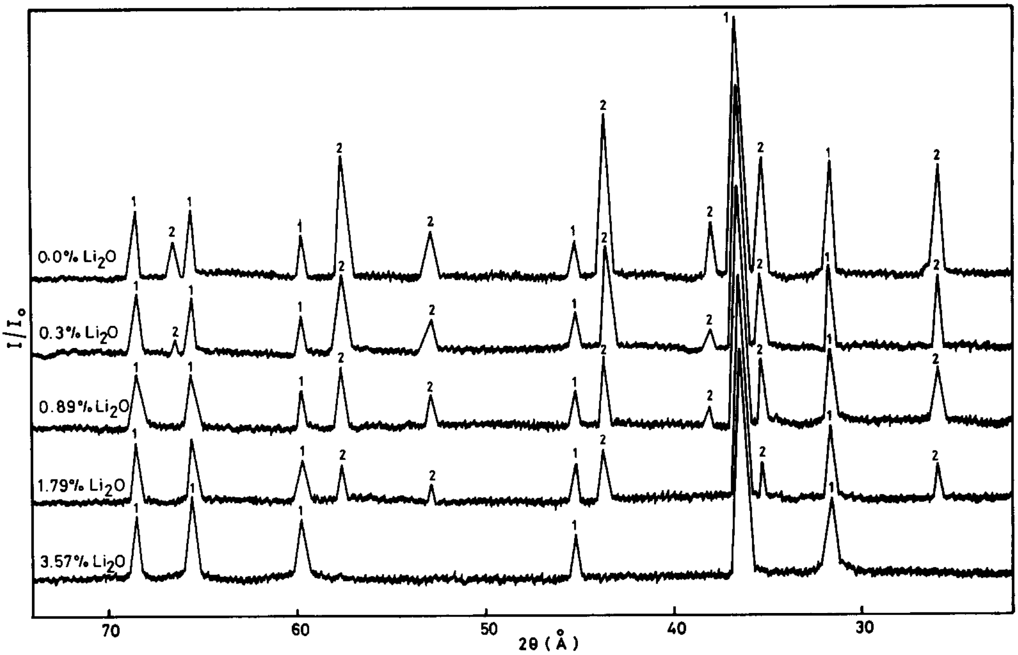

Fig. 5. XRD patterns of pure and doped solids prefired at 1000 °C: 1, $CuAl_2O_4$ phase; 2, α-Al_2O_3 (corundum) phase.

formation of α-alumina at 900 °C is similar to that observed for Na_2O doping [22]. This behaviour can be attributed to the coating of the doped aluminas with $LiAl_5O_8$ which hinders the transformation of the free alumina phase (not contributing to the formation of lithium aluminate) into α-Al_2O_3 or any other crystalline form. The fact that very well-crystallized α-alumina is formed in the pure mixed solid sample preheated at 900 °C clearly indicates the role of CuO in promoting or catalysing the crystallization process of the α-Al_2O_3 phase. α-Alumina is normally formed by heating the unloaded pure Al_2O_3 sample at temperatures greater than 1000 °C [23]. An increase in the precalcination temperature of various doped CuO–Al_2O_3 solids above 900 °C may result in the crystallization of the α-alumina phase.

Figure 5 shows the X-ray diffractograms of pure and doped solids precalcined in air at 1000 °C. It can be observed from Fig. 5 that the pure CuO–Al_2O_3 sample (1000 °C) consists of a mixture of very well-crystallized copper aluminate and α-Al_2O_3 (corundum). This finding clearly indicates the role of the CuO phase (16.3 wt.%) in promoting the crystallization of Al_2O_3 into α-alumina at 1000 °C. It can also be seen from Fig. 5 that the addition of a small amount of Li_2O (0.30 wt.%) to the alumina support specimen results in a very significant decrease in the relative intensities of all the diffraction lines of both the α-Al_2O_3 and $CuAl_2O_4$ phases. The increase in the amount of dopant oxide added in the range 0.30–1.79 wt.% Li_2O

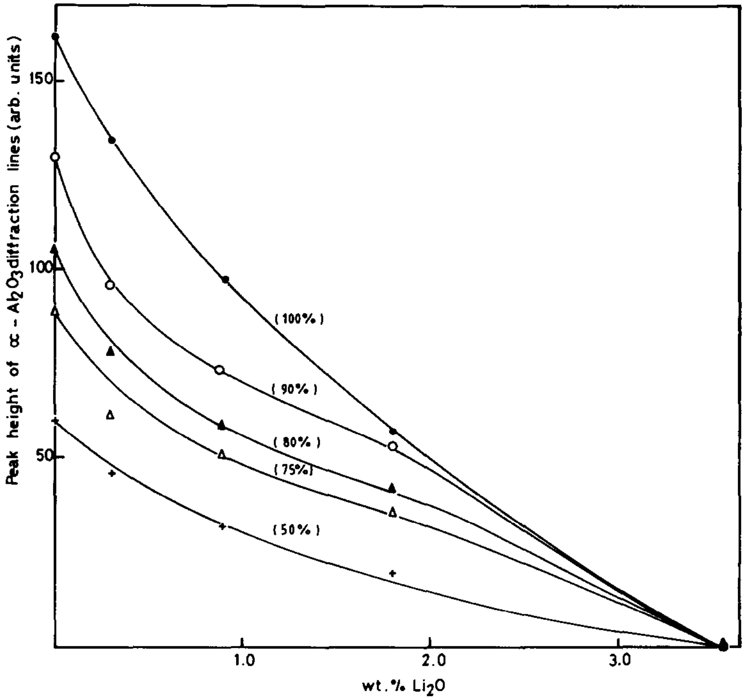

Fig. 6. Effect of Li_2O content on the peak height of the diffraction lines of α-Al_2O_3 produced at 1000 °C.

leads to a progressive decrease in the relative intensities of the diffraction lines of the α-Al_2O_3 phase produced. The effect of Li_2O doping of Al_2O_3 on its crystallization to α-alumina is better indicated by Fig. 6 which shows the peak heights of the main lines of 100%, 90%, 80%, 75% and 50% of α-alumina. This figure shows that the presence of 3.57 wt.% Li_2O results in the complete disappearance of all the diffraction lines of the α-Al_2O_3 phase. In other words, the catalysing effect of CuO in the crystallization of α-alumina at 1000 °C is counteracted by doping with 3.57 wt.% Li_2O. Similar results have been reported in Na_2O doping of CuO–Al_2O_3 solids [22]. However, the effect of Li_2O is more pronounced than that of Na_2O. The observed inhibiting effect of Li_2O on the crystallization of α-Al_2O_3 can be attributed to the formation of $LiAl_5O_8$ which takes place at about 600 °C and which covers the surfaces of the Al_2O_3 grains thus preventing the crystallization process even when heating at 1000 °C. It is worth mentioning here that the doped alumina support in the CuO–Al_2O_3 solid precalcined at elevated temperature (1000 °C) remains as an amorphous phase. This phenomenon is very desirable in the field of catalysis, because the catalytic activity of amorphous alumina is much better than that of α-Al_2O_3 [24]; in addition, the dispersion power of the amorphous alumina support is much greater than that of the crystalline form (dispersion is the capability of the

Al_2O_3 support to increase the surface concentration of the loaded oxide which acts as a catalyst [32].

CONCLUSIONS

The main conclusions that can be derived from the experimental results are as follows.

(1) Lithium oxide doping of $CuO-Al_2O_3$ solids at 500 °C results in the location of the Li^+ ions in the octahedral and tetrahedral sites of the Al_2O_3 support. This process enhances the crystallization of the CuO phase and is normally accompanied by a significant decrease in the dispersion capacity of Al_2O_3 for CuO.

(2) Li_2O doping at 800 °C inhibits the solid–solid interactions between CuO and Al_2O_3 which yield $CuAl_2O_4$ due to the formation of $LiAl_5O_8$ and an Li_2O-CuO solid solution.

(3) Copper oxide (16.3 wt.%) loaded on an alumina support enhances its crystallization into α-Al_2O_3 (corundum) at 900–1000 °C, whereas Li_2O treatment inhibits this process to an extent proportional to the amount of lithium oxide added. The addition of 1.79 wt.% Li_2O is sufficient to prevent the formation of α-Al_2O_3 at 900 °C, whereas at 1000 °C the amount required is increased to 3.57 wt.%. In other words, the addition of 3.57 wt.% Li_2O leads to the formation of an amorphous alumina even when heating at 1000 °C.

REFERENCES

1 M. Samaane and S.J. Teichner, Bull. Soc. Chim. Fr., 10 (1968) 1927, 1934, 1944.
2 D. Dollimore and T.E. Jones, J. Appl. Chem. Biotechnol., 23 (1973) 137.
3 E.M. Ezzo, G.A. El-Shobaky and M.M. Selim, Surf. Technol., 10 (1980) 47.
4 G. Wendt, E. Fritsch and R. Schöliner, React. Kinet. Catal. Lett., 16 (1981) 137.
5 A. Lycourghiotis, D. Vattis, G. Karaiskakis and N. Katsonos, J. Less-Common. Met., 86 (1982) 137.
6 G.A. El-Shobaky, Th. El-Nabarawy, I. Morsi and N. Ghoneim, Surf. Technol., 19 (1983) 109.
7 G.A. El-Shobaky and A. Al-Noaimi, Surf. Technol., 26 (1985) 117, 235.
8 G.A. El-Shobaky, G.A. Fagal and T. Saber, Bull. Soc. Chim. Fr., 4 (1987) 547.
9 G.A. El-Shobaky, G.A. Fagal, N. Petro and A.N. Dessouki, Radiat. Phys. Chem., 29 (1987) 39.
10 G.A. El-Shobaky, Th. El-Nabarawy and G.A. Fagal, Radat. Phys. Chem., 32 (1988) 773.
11 M.Lo. Jacono, M. Schiavello and A. Cimino, J. Phys. Chem., 75 (1971) 1044.
12 M.Lo. Jacono, A. Cimino and G.C.A. Schuit, Gazz. Chim. Ital., 105 (1973) 1281.
13 M.Lo. Jacono, M. Schiavello, D. Cordischi and G. Mercati, Gazz. Chim. Ital., 105 (1975) 1165.
14 A. Lycourghiotis, A. Tsiatsios and N.A. Katsanos, Z. Phys. Chem., 126 (1981) 95.

15 J. Leyrer, B. Vielhaber, M.I. Zaki, Z. Shuxian and H. Knözinger, Mater. Chem. Phys., 13 (1985) 301.
16 G.A. El-Shobaky, G.A. Fagal and T. Saber, Bull. Soc. Chim. Fr., 4 (1987) 551.
17 A. Lycourghiotis, C. Defosse and B. Delmon, Rev. Chim. Miner., 16 (1979) 473.
18 M. Houalla, F. Delanary and B. Delmon, J. Phys. Chem., 85 (1981) 1704.
19 R.L. Chin and D.M. Hercules, J. Catal., 74 (1982) 121.
20 X. Youchang, Q. Minxie and T. Youqi, Sci. Sin., 27 (1984) 549.
21 G.A. El-Shobaky and A. Al-Noaimi, Bull. Soc. Chim. Fr., 4 (1987) 544.
22 G.A. El-Shobaky, Th. El-Nabarawy, G.A. Fagal and N.H. Amin, Thermochim. Acta, 5483.
23 J. Zemlica and C. Barta, Cryst. Res. Technol., 7 (1972) 965.
24 J. Leyrer, M.I. Zaki and H. Knözinger, J. Phys. Chem., 90 (1986) 4775.
25 Y. Liu, Y. Xie, J. Ming, J. Lin and Y. Tang, Cuihua Xuebao, 3 (1982) 262.
26 J. Haber, Pure Appl. Chem., 56 (1984) 1663.
27 J. Haber, T. Machej and T. Czeppe, Surf. Sci., 151 (1985) 301.
28 G.A. El-Shobaky and I.F. Hewaidy, Bull. Natl. Res. Centre, Cairo, 6 (1981) 209.
29 G.A. El-Shobaky, K. El-Barawy, A. Ibrahim and I.F. Hewaidy, Bull. Natl. Res. Centre, Cairo, 10 (1985) 246.
30 M. Houalla, J. Lemaitre and B. Delmon, J. Chem. Soc., Faraday Trans. 1, 78 (1982) 1389.
31 F.A. Kröger, Chemistry of Imperfect Crystals, North-Holland, Amsterdam, 1964.
32 G.R. Gavalas, C. Phichitkul and G.E. Voecks, J. Catal., 88 (1984) 54, 65.