

Solid–solid interaction in CuO–ZnO/Al₂O₃ system under varying conditions

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Abstract

A series of pure and Li₂O-doped CuO–ZnO/Al₂O₃ mixed solids was prepared by wet impregnation of finely powdered Al(OH)₃ with Zn(NO₃)₂ and Cu(NO₃)₂ solutions. The doped solids were treated with LiNO₃ solution prior to treatment with zinc and copper nitrate solutions. The amount of zinc oxide varied between 0.0 and 7.7 wt.% and that of copper oxide between 15 and 16.3 wt.%. The solid–solid interactions between the different constituents were investigated using TG, DTG and DTA of uncalcined solids and XRD of the solids calcined at 400–1000°C.

The results revealed that Al(OH)₃ undergoes dehydroxylation in different steps starting from 206°C and the removal of last traces of OH groups strongly bound to Al₂O₃ lattice occurs at 396–496°C. Copper and zinc nitrates decompose simultaneously at 165–216°C, forming the corresponding oxides. The produced CuO interacts readily with Al₂O₃, producing CuAl₂O₄ at temperatures starting from 600°C and the completion of this reaction, yielding well-crystallized CuAl₂O₄ phase, requires heating at 1000°C. Zinc oxide hinders the CuAl₂O₄ formation at 600°C and enhances this reaction at 800°C. The hindering and enhancing effects depended on the amount of zinc oxide present. Furthermore, zinc oxide hinders the crystallization of alumina into α-corundum phase by heating at 1000°C. Li₂O-doping catalyzes the crystallization of copper oxide phase by heating the supported oxides at 600°C and suppresses the solid–solid interactions between CuO and Al₂O₃ yielding CuAl₂O₄ by heating at 800°C. © 1998 Elsevier Science B.V.

Keywords: CuO–ZnO/Al₂O₃ system; Li₂O-doping; Solid–solid interaction

1. Introduction

Al₂O₃ is frequently employed as a suitable support for a large variety of catalysts used in various chemical reactions [1–7]. However, these catalysts are liable to deactivation due to the formation of aluminate compounds via metal oxide–alumina interactions [8]. It

has been reported that the rate of reaction between metal oxides and Al₂O₃ descends in the following order CuO>CoO>NiO>Fe₂O₃ [9]. The strong metal oxide–Al₂O₃ interactions in CuO/Al₂O₃ system justifies the necessity of addition of other oxides to suppress these interactions [2,3]. ZnO is often added to fulfill this task. The solid–solid interactions between transition metal oxides and alumina are the focus of interest of several investigators [8–17]. These authors claimed that, besides the aluminate formation,

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transition-metal oxides catalyze the phase transformation of γ -Al₂O₃ into κ -, θ - and α -aluminas [12–18].

The present work aimed at investigating the role of calcination temperature and Li₂O-doping on solid–solid interactions in CuO–ZnO/Al₂O₃ used in the catalysis of CO oxidation by O₂ and in low-temperature CO conversion by steam. The techniques employed were TG, DTG, DTA and XRD.

2. Experimental details

2.1. Materials

Pure CuO–ZnO/Al₂O₃ samples were prepared by treating a known mass of finely powdered Al(OH)₃ with a solution containing a calculated amount of Zn(NO₃)₂·6H₂O, drying at 100°C followed by calcination at 500°C for 5 h. The obtained solid was treated with Cu(NO₃)₂ dissolved in the least amount of distilled water, dried at 100°C and heated in air at 400–1000°C for 5 h. The amount of zinc oxide was 0.0, 0.83, 1.96, 3.86 and 7.7 wt.%. The prepared samples which include the previously mentioned ZnO contents were designated CuAl, CuZnAl-I, CuZnAl-II, CuZnAl-III and CuZnAl-IV. These samples contain 16.3, 16.2, 16, 15.7 and 15.1 wt.% CuO, respectively.

Li₂O-doped mixed solids were prepared by treating a known mass of finely powdered Al(OH)₃ with LiNO₃ solution, drying at 100°C, then treating with Zn(NO₃)₂ and Cu(NO₃)₂ solutions. The obtained solids were dried at 100°C and calcined at 600°, 800° and 1000°C for 5 h. The amount of CuO and ZnO in the doped samples were 15.7 and 3.86 wt.%, respectively. The dopant concentration was 0.13, 0.27, 0.54, 1.08 and 1.63 wt.% Li₂O. All the employed chemicals Al(OH)₃, Zn(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O and LiNO₃ were of analytical grade supplied by Prolabo and BDH.

TG, DTG and DTA analyses of various uncalcined materials were done using a Perkin–Elmer thermal analyzer (DT-7/Unix system). An 8-mg solid portion was taken in each DTA measurement and 18 mg in each TG measurement. The reference material was α -Al₂O₃ (corundum). The rate of heating was kept at 20°C min⁻¹ and all the measurements were carried out in a current of N₂ flowing at a rate of 50 cm³ min⁻¹.

The X-ray powder diffraction patterns of the various calcined samples were measured using a Philips diffractometer (Type PW 1390). The patterns were run with nickel-filtered CuK α -radiation (λ =1.5405 Å) at 36 kV and 16 mA at a scanning rate of $2\theta=2^\circ$ min⁻¹.

3. Results and discussion

3.1. Thermal behaviour of uncalcined Li-free mixed solids

TG, DTG and DTA curves of uncalcined mixed solids were determined and the results obtained are summarized in Tables 1 and 2. Representative TG, DTG and DTA curves are illustrated in Fig. 1 for CuZnAl-III. The DTA curves display four endothermic peaks at 115–184, 205–252, 250–289 and 300–

Table 1
DTA results for uncalcined Li-free solid samples

Solid	$\Delta T/T$	$T_{\max}/^\circ\text{C}$
CuAl	endo, s ^a	117
	endo, s ^a	252
	endo, s ^a	285
	endo, vs ^b	308
CuZnAl-I	endo, w ^c	157
	endo, s ^a	248
	endo, s ^a	286
	endo, vs ^b	300
CuZnAl-II	endo, w ^c	120
	endo, s ^a	149
	285	189
	endo, vs ^b	301
CuZnAl-III	endo, s ^a	115
	endo, w ^c	205
	endo, s ^c	250
	endo, vs ^b	302
CuZnAl-IV	endo, w ^c	184
	endo, w ^c	205
	endo, s ^a	252
	endo, vs ^b	306

^a Strong peaks.

^b Very strong peaks.

^c Weak peaks.

Table 2
TG and DTG results for uncalcined Li-free solid samples

Solid	Temperature range/°C	WL. %
CuAl	Room temperature–121	4.9
	164–223	12.0
	223–285	16.9
	285–500	5.5
CuZnAl-I	Room temperature–155	4.5
	155–218	11.4
	218–281	17.6
	281–500	5.9
CuZnAl-II	Room temperature–165	6.0
	165–226	13
	226–282	15.7
	282–500	5.8
CuZnAl-III	Room temperature–137	6.5
	137–216	14.4
	216–251	12.8
	251–500	6.7
CuZnAl-IV	Room temperature–157	6.0
	157–217	13
	217–254	14.7
	254–500	6.7

308°C. The TG and DTG curves exhibit four successive weight-loss (WL) processes as shown in Table 2.

The first set of endothermic peaks (Table 1) correspond to removal of physisorbed water and water of crystallization of copper and zinc nitrates. The second and third sets of endothermic peaks indicate thermal decomposition of copper and zinc nitrates, respectively, to produce the corresponding oxides. The last set of endothermic peaks characterizes dehydroxylation of $\text{Al}(\text{OH})_3$ producing Al_2O_3 .

The absence of any thermal effect in the DTA curves at temperatures between 500° and 1000°C does not exclude the possibility of solid–solid interactions in the test materials. It seems that these reactions take place at an extremely low rate which makes their detection by DTA a difficult task.

4. XRD of calcined mixed oxides

4.1. Li-free mixed oxides

X-ray powder diffractograms of various mixed solids preheated in air at 400°C were measured (not given). These diffractograms show that the test solids consist of well-crystallized CuO phase together with poorly crystalline $\gamma\text{-Al}_2\text{O}_3$ [19]. The addition of ZnO up to 1.96 wt.% to CuO/ Al_2O_3 mixed solids did not lead to any appreciable change in the diffractogram of

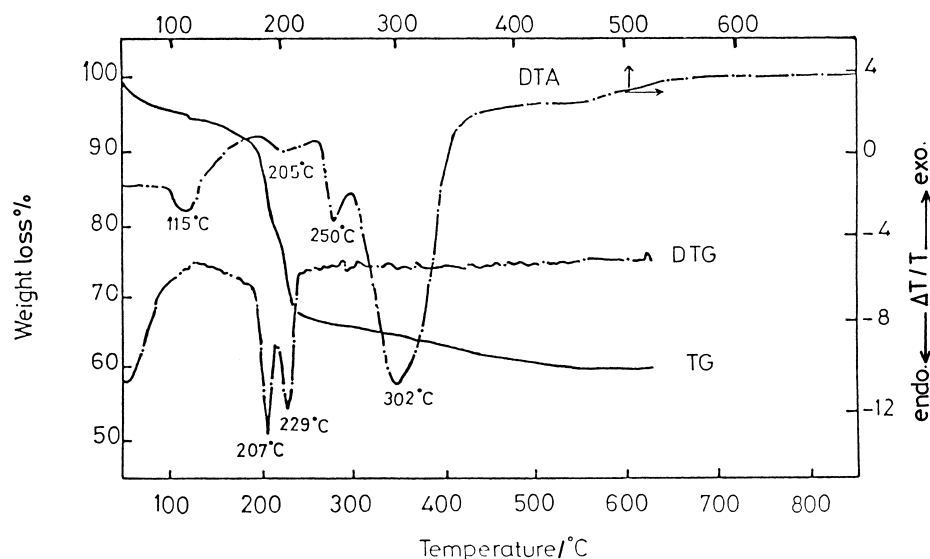


Fig. 1. Thermograms of uncalcined CuZnAl-III.

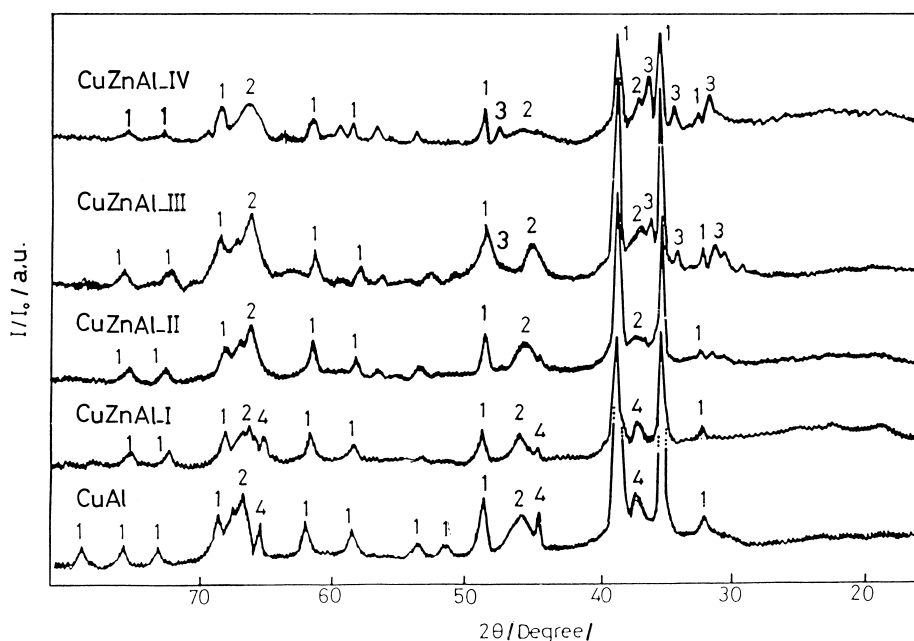


Fig. 2. XRD of different Cu–Zn/Al mixed solids preheated in air at 600°C: (1) CuO; (2) γ -Al₂O₃; (3) ZnO; and (4) CuAl₂O₄.

the mixed solid. Increasing the amount of ZnO above this limit led to the appearance of the diffraction lines of a separate ZnO phase. So, the endothermic peaks observed in the DTA curves of the different investigated solids at temperatures up to 400°C indicate the thermal decomposition of Al(OH)₃, Cu(NO₃)₂ and Zn(NO₃)₂ to produce poorly crystalline γ -Al₂O₃, CuO and ZnO phases.

The rise in the calcination temperature of the different mixed oxides above 400°C may lead to possible solid–solid interactions between CuO and Al₂O₃, producing CuAl₂O₄ [15,20]. Fig. 2 shows X-ray diffractogram of the test solids preheated in air at 600°C. The comparison between the diffractogram of zinc oxide-free sample and those containing different amounts of ZnO reveals the following:

1. The zinc oxide-free sample consists entirely of well-crystallized CuO phase, together with CuAl₂O₄ with moderate crystallinity and poorly crystalline γ -Al₂O₃.
2. The presence of ZnO resulted in weakening the intensity of diffraction lines due to the CuO phase to an extent proportional to its amount present, and

to a decrease in the intensity of the diffraction lines of CuAl₂O₄ phase.

3. The addition of 7.71 wt.% of ZnO prevented completely the formation of copper aluminate and resulted in the presence of a portion of ZnO as a separate phase.

It can thus be concluded that zinc oxide hinders the solid–solid interaction between CuO and Al₂O₃ at 600°C to form copper aluminate and decreases the crystallinity of CuO which might be taken as an evidence for a higher degree of dispersion of CuO in the material.

The rise in calcination temperature of the test solids to 800°C brought about significant changes in the diffractograms as seen from Fig. 3. Inspection of Fig. 3 reveals the following:

1. CuAl preheated at 800°C consists of a mixture of CuO, CuAl₂O₄ and poorly crystalline γ -alumina.
2. The addition of ZnO (0.83–7.71 wt.% ZnO) results in a progressive increase in the intensity of the diffraction lines relative to CuAl₂O₄ to an extent proportional to its amount.

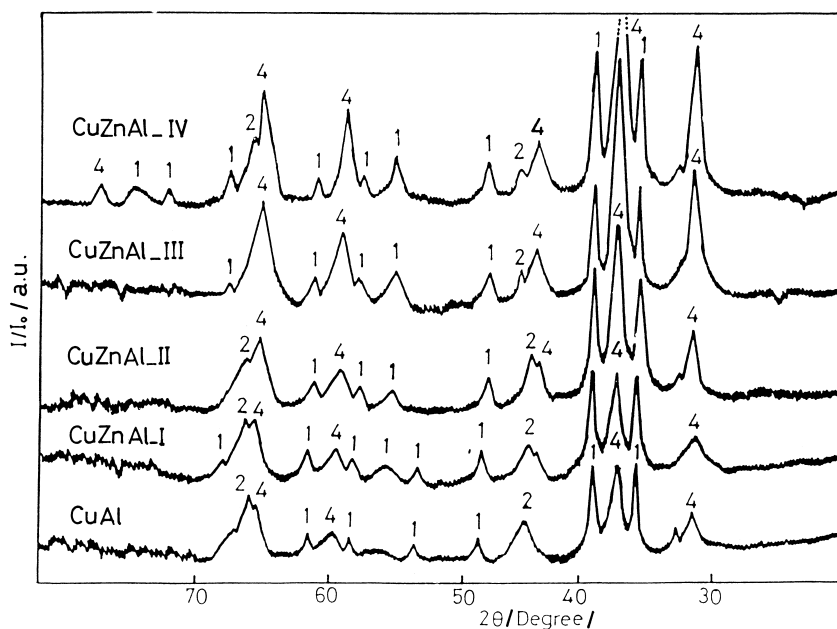


Fig. 3. X-ray diffractograms of $\text{CuO}/\text{Al}_2\text{O}_3$ containing different amounts of ZnO preheated in air at 800°C : (1) CuO; (2) $\gamma\text{-Al}_2\text{O}_3$; and (4) CuAl_2O_4 .

These results clearly indicate that ZnO stimulates the solid–solid interaction between CuO and Al_2O_3 , forming CuAl_2O_4 by heating in air at 800°C . Thus, ZnO behaves in a manner opposite to that manifested at 600°C . In other words, suppression of CuAl_2O_4 formation was observed by heating at 600°C , while enhancement of this phase was observed by heating at 800°C . These results point out to the role of calcination temperature in solid–solid interactions between CuO and Al_2O_3 in the presence of small amounts of ZnO.

Fig. 4 shows the diffractograms of different investigated solids, preheated at 1000°C . Inspection of Fig. 4 reveals the following:

1. Heating CuAl at 1000°C results in a complete conversion of CuO into a well-crystallized copper aluminate and subsequent transformation of $\gamma\text{-Al}_2\text{O}_3$ into well-crystallized $\alpha\text{-Al}_2\text{O}_3$ (corundum).
2. The addition of different amounts of ZnO (0.83–7.71 wt.%) did not affect the solid–solid interaction leading to the formation of CuAl_2O_4 .
3. On the other hand, ZnO brought about a progressive decrease in the intensity of the diffraction lines

due to $\alpha\text{-Al}_2\text{O}_3$ to an extent proportional to its amount. In fact, the height of the main line of $\alpha\text{-Al}_2\text{O}_3$ (2.09 \AA) decreases from 110, 95, 90, 63 and 46 (arbitrary units) due to the presence of 0.0, 0.83, 1.96, 3.86 and 7.71 wt.% ZnO, respectively.

4. No single diffraction line due to ZnAl_2O_4 was detected in the diffractograms of $\text{CuO}/\text{Al}_2\text{O}_3$ containing 3.86 and 7.71 wt.% ZnO. It seems that some of ZnO added dissolved in CuO and/or CuAl_2O_4 forming solid solutions and the other portion might cover the surfaces of Al_2O_3 particles.

The absence of any effect of ZnO on solid–solid interactions between CuO and Al_2O_3 at 1000°C forming CuAl_2O_4 seems to be expected since the calcination temperature was high enough to affect the completion of the $\text{CuO} + \text{Al}_2\text{O}_3 \rightarrow \text{CuAl}_2\text{O}_4$ reaction.

The suppression of crystallization of $\alpha\text{-Al}_2\text{O}_3$ in $\text{CuO}/\text{Al}_2\text{O}_3$ being treated with ZnO and preheated at 1000°C might result from coverage of its surfaces with ZnO film acting as an energy barrier opposing the crystallization process of α -alumina.

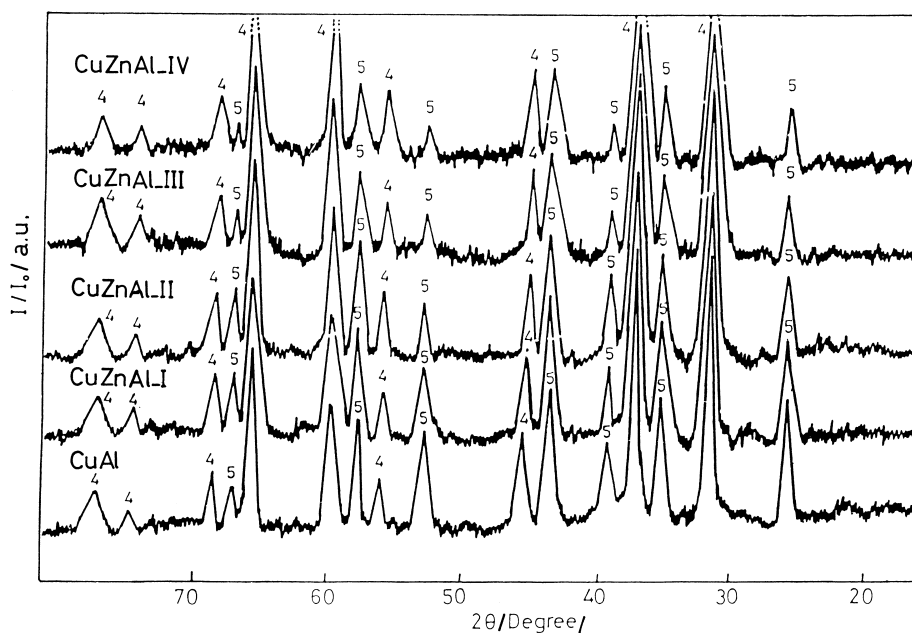


Fig. 4. X-ray diffractograms of $\text{CuO}/\text{Al}_2\text{O}_3$ containing different amounts of ZnO preheated in air at 1000°C : (4) CuAl_2O_4 ; and (5) $\alpha\text{-Al}_2\text{O}_3$.

5. Li_2O -doped mixed solids

X-ray diffractograms of Li-treated solids calcined at 600°C were measured. These diffractograms (not given) show that these solids consist of poorly crystalline CuO phase and its degree of crystallinity increases on increasing the dopant concentration. This finding suggests that Li_2O -doping enhances the degree of ordering of CuO phase to an extent proportional to the amount of dopant present. The ordering of CuO crystallites due to doping may be reflected as a decrease in the dispersivity of copper oxide phase. Hence, the doping process may lead to a decrease in the degree of dispersion of CuO present in the mixed solid specimens. It is known that Al_2O_3 support has the ability to disperse transition-metal oxides on its surface. It seems that the added lithium oxide, which was retained on the alumina surface, hindered the uptake of CuO on its surface leading to aggregation or crystallization of CuO crystallites into a well-ordered CuO phase. In fact, the added lithium oxide can be located on octa- and tetrahedral sites of the treated Al_2O_3 , thus decreasing its capacity towards copper oxide uptake. This process is normally accom-

panied by aggregation of CuO forming a well-ordered CuO phase [15].

Fig. 5 shows that pure mixed solids, and those treated with 0.13 wt.% Li_2O , being calcined at 800°C were converted entirely into copper aluminate compound having a reasonable degree of crystallinity. It can also be seen from Fig. 5 that the increase in the dopant concentration resulted in a progressive suppression of copper aluminate formation, i.e. Li_2O -doping hinders solid–solid interactions between CuO and Al_2O_3 to an extent proportional to its amount present.

Li_2O added may interact with Al_2O_3 forming lithium aluminate [15,21] which covers the surfaces of the alumina particles hindering the thermal diffusion of copper oxide towards its interior. Hence, the formed lithium aluminate film suppresses the diffusion of copper species in the bulk of Al_2O_3 . The fact that the diffraction lines of lithium aluminate were not detected in the XRD patterns of Li_2O -doped samples calcined at 800°C may indicate its presence in the amorphous state or that its amount is too small (1.63 wt.%) to be detected by XRD.

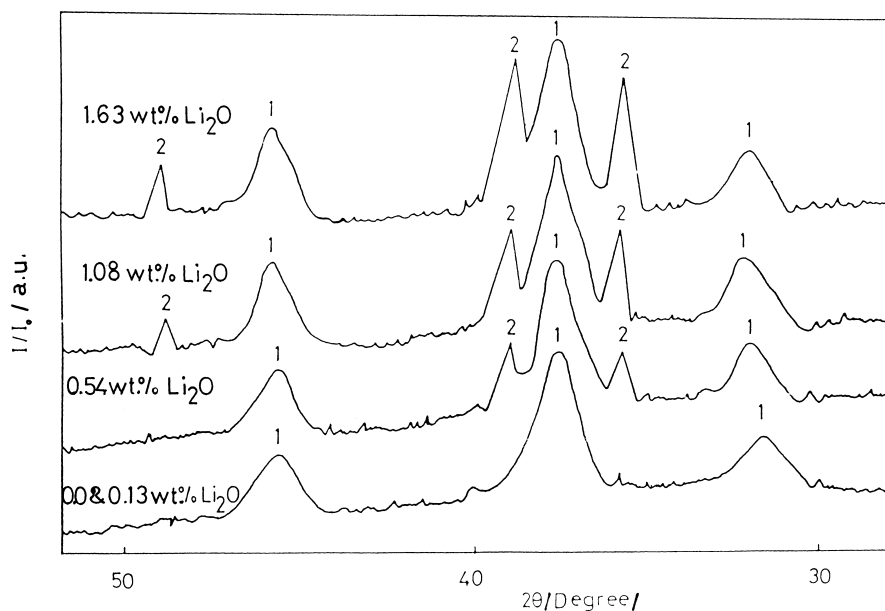


Fig. 5. XRD patterns of pure and doped solids precalcined at 800°C. (1) CuAl₂O₄; and (2) CuO phases.

6. Conclusions

The following are the main conclusions that can be drawn from the results obtained:

1. Copper oxide interacts with Al₂O₃ at $\geq 600^\circ\text{C}$ to produce CuAl₂O₄ phase with moderate crystallinity. The complete conversion of CuO into well-crystallized copper aluminate takes place at 1000°C.
2. ZnO hinders the solid–solid interaction, taking place at 600°C, between CuO and Al₂O₃ to produce CuAl₂O₄. An opposite effect was observed upon heating at 800°C. The hindrance and stimulation effects of ZnO towards CuAl₂O₄ formation at 600 and 800°C, respectively, ran parallel to its amount present.
3. ZnO hinders the crystallization process $\gamma\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$ in CuO–ZnO/Al₂O₃ mixed solids precalcined at 1000°C to an extent proportional to its amount added.
4. Li₂O doping of CuO–ZnO/Al₂O₃ system preheated at 600°C, improves the degree of ordering of CuO crystallites. In other words, Li₂O decreases the dispersivity of CuO crystallites and suppresses

solid–solid interaction $\text{CuO} + \text{Al}_2\text{O}_3 \rightarrow \text{CuAl}_2\text{O}_4$ taking place at 800°C.

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