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Thermal solid–solid interaction and catalytic properties of CuO/Al_2O_3 system treated with ZnO and MoO_3

W.M. Shaheen*

Laboratory of Surface Chemistry, Department of Physical Chemistry, National Research Center, El-Tahrir Street, Dokki, Cairo, Egypt

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Abstract

The effect of ZnO (1.70–12.13 wt.%) and MoO_3 (2.96–19.63 wt.%) treatment on thermal solid–solid interaction and physicochemical properties of $0.20CuO/Al_2O_3$ system was investigated. The pure and treated mixed solids were subjected to heat treatment at 400–1000 °C. The thermal behavior of these solids was studied by TG and DTA techniques. The thermal products were characterized using X-ray diffraction (XRD) analysis. The catalytic behavior of all solids was tested in hydrogen peroxide (H_2O_2) decomposition reaction at 30–50 °C. The results revealed that crystalline γ-Al_2O_3 phase were detected in all solids preheated at 400–800 °C with no diffraction lines from the CuO phase. Crystalline $CuAl_2O_4$ phase formed as a result of solid–solid interaction between CuO and Al_2O_3 at 800 °C. The treatment of pure solids with MoO_3 hindered the formation of $CuAl_2O_4$ phase because of the formation of copper molybdate phase while the treatment with ZnO had the opposite effect and might form solid solutions of formula $(Zn_xCu_{1-x})Al_2O_4$ at 800 and 1000 °C. Furthermore, MoO_3 enhanced the crystallization of γ-Al_2O_3 into α-Al_2O_3 at 1000 °C. The catalytic activity of pure solids treated with MoO_3 or ZnO and preheated at 400 and 600 °C increased up to 10.88 wt.% MoO_3 and up to 3.34 wt.% ZnO. The observed increase in activity is attributed to increasing concentration of catalytically active constituents and/or formation of new active sites. The activity progressively decreased with increasing treatment temperature up to 1000 °C and with increasing concentration of MoO_3 and ZnO up to 19.63 and 12.13 wt.%, respectively. The decreasing in activity is due to the formation of inactive compounds such as $(Zn_xCu_{1-x})Al_2O_4$, MoO_3, α-Al_2O_3 and/or sintering processes. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: CuO/Al_2O_3; Doping; Solid–solid interaction; Catalytic activity

1. Introduction

The catalytic activity and selectivity of a large variety of solids can be modified by treating them with small amount of foreign oxides [1,2]. This treatment induces significant changes in the physicochemical characteristics of the treated solids such as the electrical, magnetic, textural and acidity features of the resulting solid catalysts [3,4]. The binary oxides are widely used in the field of catalysis [5–7]. Copper oxide supported on alumina system is one of the most important catalysts used for several organic and inorganic catalytic reactions [8–10]. The addition of small amounts of certain foreign cations such as Li^+, Na^+ and Sr^{2+} to the system has found to influence the mutual solid–solid interaction between the constituents [11,12]. This influence may be accompanied by significant changes in the catalytic and physicochemical properties of the doped support catalysts [13,14].

This work reports a study the effects of ZnO and MoO_3 treatment on thermal solid–solid interaction and physicochemical properties of CuO/Al_2O_3 system

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* Fax: +20-2-337-0931.
E-mail address: shaheen40@hotmail.com (W.M. Shaheen).

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at treatment temperature ranged between 400 and 1000 °C. The techniques employed were thermal analysis, i.e. TG and DTA, X-ray diffraction (XRD) analysis and decomposition of hydrogen peroxide (H_2O_2) in aqueous solution at 30–50 °C.

2. Experimental

2.1. Materials

Aluminum hydroxide of analytical grade was supplied by Prolabo Company. A known mass of finely powdered $Al(OH)_3$ was impregnated with a solution containing definite amount of copper nitrate trihydrate, $Cu(NO)_3{\cdot}3H_2O$, corresponding to CuO. The extent of copper oxide was fixed at 13.5 wt.% for all solids prepared. The paste obtained was dried at 100 °C overnight then thermally treated at 400, 600, 800 and 1000 °C for 4 h in air. The nominal composition of the calcined solids was $0.20CuO/Al_2O_3$. The mixed solids were prepared by treating a known mass of $Al(OH)_3$ with solutions containing different proportions of $Zn(NO_3)_2{\cdot}6H_2O$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, separately. The pastes obtained were dried at 100 °C overnight. The zinc and molybdate solutions impregnated $Al(OH)_3$ specimens were treated with solutions containing a known amount of copper nitrate solution then dried at 100 °C overnight. The mixed solids obtained were thermally treated at 400, 600, 800 and 1000 °C. The amount of zinc nitrate tetrahydrate was expressed in wt.% ZnO were 1.70, 3.34, 6.46 and 12.13. On the other hand, the amounts of ammonium molybdate expressed as wt.% MoO_3, were 2.96, 5.76, 10.88 and 19.63. The nitrate salts were of analytical grade supplied by BHD Company.

2.2. Techniques

Thermal analysis (TG–DTA) was performed in air atmosphere using Shimadzu DT-40 thermal analyzer at flowing rate of 30 cm^3/m. The heating rate was fixed at 15 $°C\,min^{-1}$.

XRD bands were obtained at the room temperature using a Philips X-ray diffractometer (Goniometer PW 1390), employing Cu Kα radiation as the X-ray source. The X-ray tube was operated at 36 kV and 16 mA. The samples were finely ground and packed in a plastic holder. The diffraction angle 2θ was scanned at a rate of 2°/min.

The catalytic activities of all samples were determined using the decomposition of H_2O_2 in aqueous solution at 30–50 °C. The kinetics of the decomposition was followed by a gasometric measurement of the evolved oxygen. Details of experimental method have been given elsewhere [7].

3. Results and discussion

3.1. Thermal analysis of uncalcined pure mixed solids

Fig. 1(a) shows the TG and DTA behavior of the uncalcined mixed solids having the formula $0.20Cu(NO_3)_2{\cdot}3H_2O/2Al(OH)_3$ The DTA-response shows three endotherms, their minima being located at 115, 265 and 300 °C. The TG consisted of three weight loss processes at temperatures ranged between 50 and 120 °C, 190 and 300 °C, and 300 and 500 °C. These processes were accompanied by total weight losses of 9.7, 30.5 and 42.5%. The first process corresponded with the melting [15] of copper nitrate and removal of water of crystallization as follows:

$$\begin{aligned}&0.2Cu(NO_3)_2\cdot 3H_2O + 2Al(OH)_3\\&\quad\rightarrow 0.1Cu_2(NO_3)_2(OH)_2 + 2Al(OH)_3\\&\qquad + 0.2NO_2 + 0.5H_2O + 0.05O_2\end{aligned}\tag{1}$$

The second process corresponds to the dehydroxylation of aluminum hydroxide to aluminum oxyhydroxide and also the decomposition of intermediate nitrate compound according to the following equation:

$$\begin{aligned}&0.1Cu_2(NO_3)_2\cdot(OH)_2 + 2Al(OH)_3\\&\quad\rightarrow 0.1CuOCuONO_3 + 2Al(OOH) + 0.1NO_2\\&\quad + 2.2H_2O\end{aligned}\tag{2}$$

The third step represented the complete decomposition of the mixture into CuO and Al_2O_3 as follows:

$$\begin{aligned}&0.1CuOCuONO_3 + 2Al(OOH)\\&\quad\rightarrow 0.2CuO + Al_2O_3 + 0.1NO_2 + H_2O\end{aligned}\tag{3}$$

At temperature above 550 °C, there was no noticeable weight change as detected from the TG-analysis

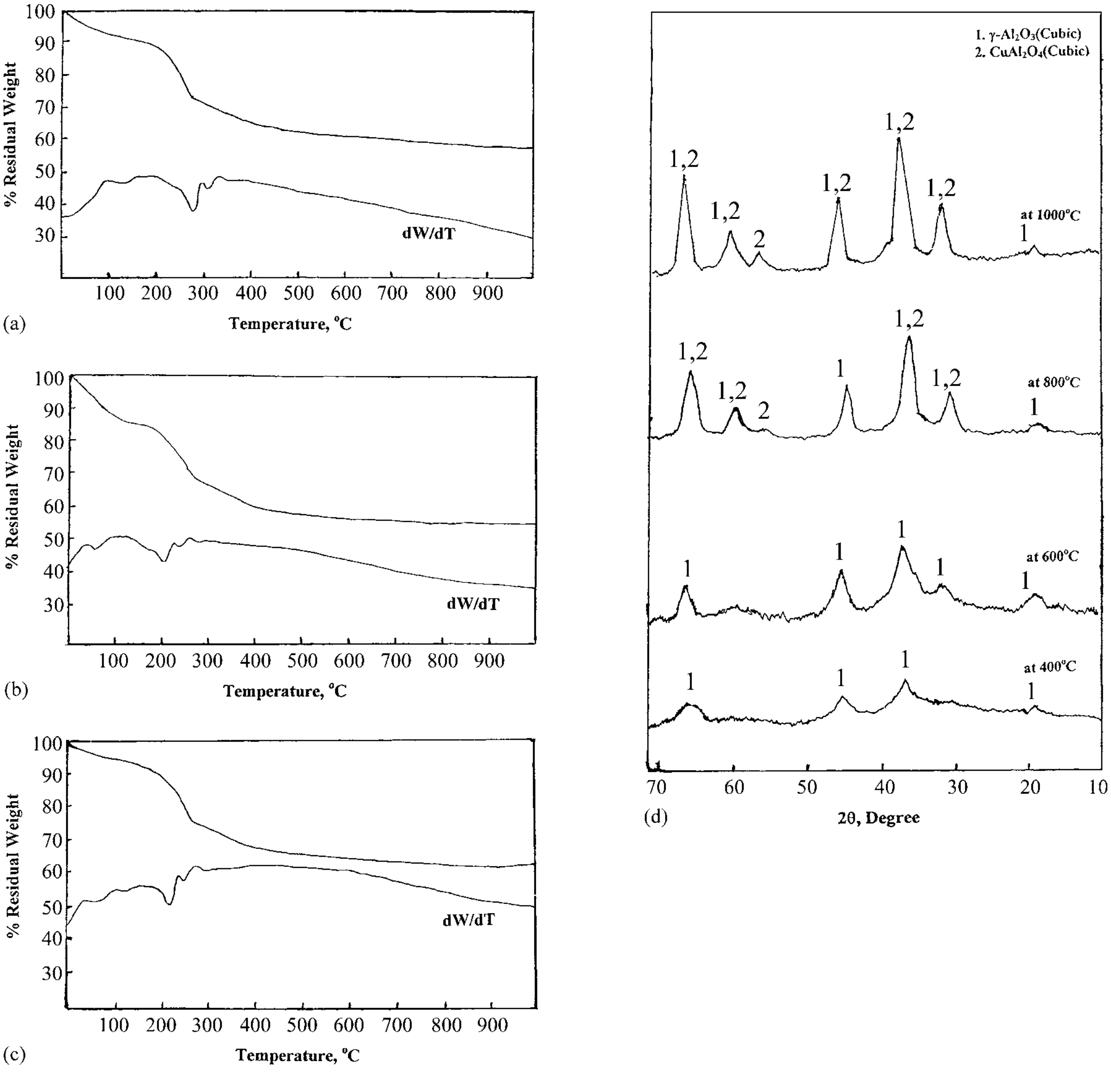

Fig. 1. (a) Thermal analysis (TG–DTA) of pure solid, $0.20Cu(NO_3)_2{\cdot}3H_2O/2Al(OH)_3$. (b) Thermal analysis (TG–DTA) of pure solid doped with 0.10ZnO. (c) Thermal analysis (TG–DTA) of pure solid doped with $0.20MoO_3$. (d) WAX diffraction of pure solid preheated at 400, 600, 800 and 1000 °C.

(cf. Fig. 1). This reflected a possible solid–solid interaction between CuO and Al_2O_3 forming copper aluminate compound [16].

3.2. Thermal analysis of uncalcined treated mixed solids

The thermograms obtained from the solid treated with zinc nitrate and ammonium molybdate, corresponding to ZnO and MoO_3 were similar to each other and that of pure solid. Two samples having the formulae $0.20Cu(NO_3)_2{\cdot}3H_2O/0.10Zn(NO_3)_2{\cdot}6H_2O/2Al(OH)_3$ and $0.20Cu(NO_3)_2{\cdot}3H_2O/(0.20/7)(NH_4)_6Mo_7O_{24}{\cdot}6H_2O/2Al(OH)_3$ were selected.

The thermograms of these samples are shown in Fig. 1(b) and (c). The first weight loss in each sample represents the loss of water of crystallization from the nitrate compounds and/or molybdate salt in the temperature range between 50 and 290 °C. Furthermore, it may represent the melting of nitrate salts as previously maintained. The complete conversion of copper nitrate, zinc nitrate and aluminum hydroxide into the corresponding CuO, ZnO and Al_2O_3 take place at about 450 °C with total weight loss of 46% which is very close to the value found theoretically. Furthermore, the thermogram of the solid treated with molybdate showed that CuO, MoO_3 and Al_2O_3 was formed at 470 °C with a total weight loss of 38% and there is no noticeable weight change observed above 500 °C up to 1000 °C.

The comparison between the thermograms of pure and treated solids represented in Fig. 1(a)–(c) showed the following points. (a) It is known that CuO decomposed to Cu_2O at temperature more than 850 °C [7]. Loss in weight and an endotherm in the DTA-curve of the investigated CuO solid normally accompany this process. However, the TG and DTA curves of the investigated solids did not include any change in weight or any endotherm at temperature more than 800 °C. This finding might suggest that CuO remained stable or interact with Al_2O_3 or MoO_3 and form copper aluminate and/or copper molybdate compounds. (b) It is known that MoO_3 melts and sublimates at about 800 °C [17–19]. This step is accompanied by a progressive weight loss on TG-curve and an endotherm in DTA-curve of the investigated MoO_3. This behavior did not noticed in our case. It seemed that MoO_3 underwent solid state interaction with CuO or Al_2O_3 or it dissolved in the matrix of alumina phase [20,21] which means that CuO/Al_2O_3 system plays as stabilizer for MoO_3 up to 1000 °C. These will be confirmed latter in the next section.

3.3. XRD investigation of pure solids fired at 400–1000 °C

Fig. 1(d) shows the X-ray diffractograms of solid Cu–Al mixtures preheated at 400, 600, 800 and 1000 °C. It can be seen that crystalline γ-Al_2O_3 (cubic) phase is detected in the solid preheated to different temperatures. Furthermore, no diffraction lines for CuO phase were detected after different treatment temperatures. This reflects the high dispersion of copper oxide crystallites on the alumina surface, which acts as a support [21]. On the other hand, the solid treated at 800 °C shows the formation of well crystalline copper aluminate phase. This phase is formed as a result of the thermal solid–solid reaction according to the following equation:

$$CuO + Al_2O_3 \rightarrow CuAl_2O_4$$

Increasing of temperature up to 1000 °C was accompanied by a progressive increase in the degree of crystallinity of $CuAl_2O_4$ phase without detection of any diffraction lines relative to CuO or Cu_2O phases.

On the other hand, the particle size of γ-Al_2O_3 and $CuAl_2O_4$ phases was calculated using the Schrer equation [22]: $d = B\lambda/\beta \cos\theta$, where d is the average particle size, B the Schrer constant (0.89), λ the wave length of X-ray beam, θ the diffraction angle of the investigated phase and β the width at half height (FWHM).

It was found that the particle size of the γ-Al_2O_3 detected at 400 °C was 36 Å while that detected at 600 °C is 41 Å. On the other hand, the particle size of $CuAl_2O_4$ phase detected at 800 °C was 60 Å while that detected at 1000 °C was 80 Å. This means that by increasing the calcination temperature the particle size of the different phases increased leading to a decrease in surface area and consequently the expecting decrease in the catalytic activity that will be discussed latter in this work.

3.4. XRD investigation of pure solid treated with ZnO and fired at 400–1000 °C

The XRD patterns of the solids treated with 1.70–12.13 wt.% ZnO and preheated at 400, 600, 800 and 1000 °C were represented on Fig. 2(a)–(d). From these figures, it can be seen that the solids treated with different proportions of ZnO and preheated at 400 and 600 °C shows only crystalline γ-Al_2O_3 phase. Its degree of crystallinity decreased for the solid doped with 3.34 wt.% ZnO then progressively increased with increasing concentration of ZnO to 12.13 wt.%.

On the other hand, it was found that the particle size of the solid preheated at 400 °C and then treated with 3.34, 6.46 and 12.13 wt.% ZnO progressively increased from (30, 39 and 43 Å) to (38, 43 and 46 Å) for those treated at 600 °C. These results means that the particle size of the detected phase decreased for solid doped with 3.34 wt.% ZnO then it significantly increased with increasing concentration of ZnO up to 12.13 wt.%. The decrease in the particle size reflected the increasing surface area of the system. This means that small amount of ZnO increased the degree of dispersion of CuO on the alumina surface and consequently will lead to an increase in activity which will be confirmed latter.

The XRD patterns of the solids treated with ZnO and preheated at 800 °C showed a well crystalline $CuAl_2O_4$ phase. The addition of 1.70–12.13 wt.% ZnO resulted in a significant increase in the intensity of the diffraction lines related to copper aluminate. Furthermore, the particle size of this phase was found to be 49, 52, 57 and 64 Å for the solids preheated at 800 °C and then treated with 3.34, 6.46 and 12.13 wt.% ZnO, respectively. These results indicate that the particle size of the detected phase progressively increased with increasing concentration of ZnO and preheated at 800 °C. On the other hand, the intensities of the diffraction line of the copper aluminate phase progressively increased with increasing calcination temperature from 800 to 1000 °C. Furthermore, the particle size of this phase progressively increased to 80, 95, 100 and 105 Å for the pure solid and those treated with 3.34, 6.46 and 12.13 wt.% ZnO and preheated at 1000 °C, respectively.

From the above results, it can be noticed that (a) ZnO stimulates the solid–solid interaction between CuO and Al_2O_3 at 800 and 1000 °C. These results point out the role of the calcination temperature in solid–solid interaction between CuO and Al_2O_3 in the presence of small amount of ZnO. (b) No diffraction lines relative to $ZnAl_2O_4$ phase were detected in the diffractograms of the solid treated with different

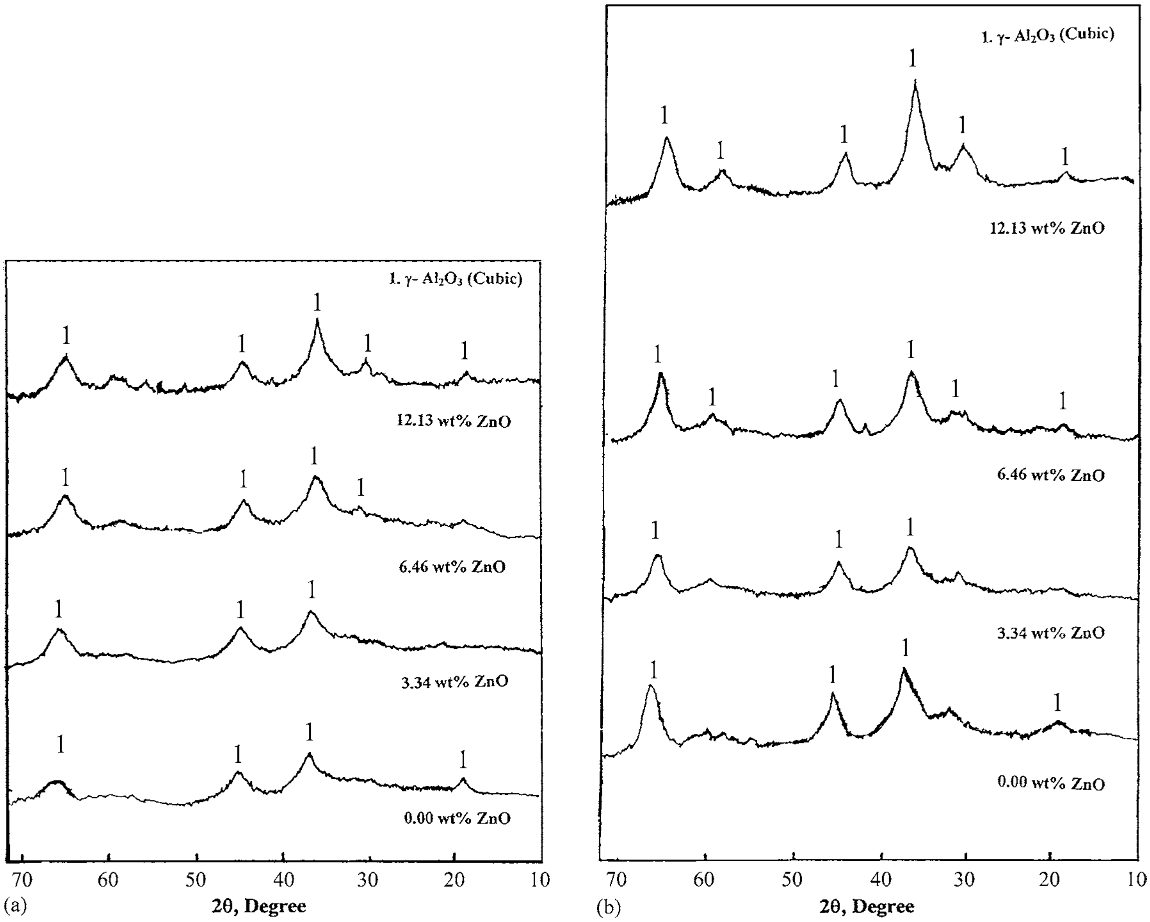

Fig. 2.

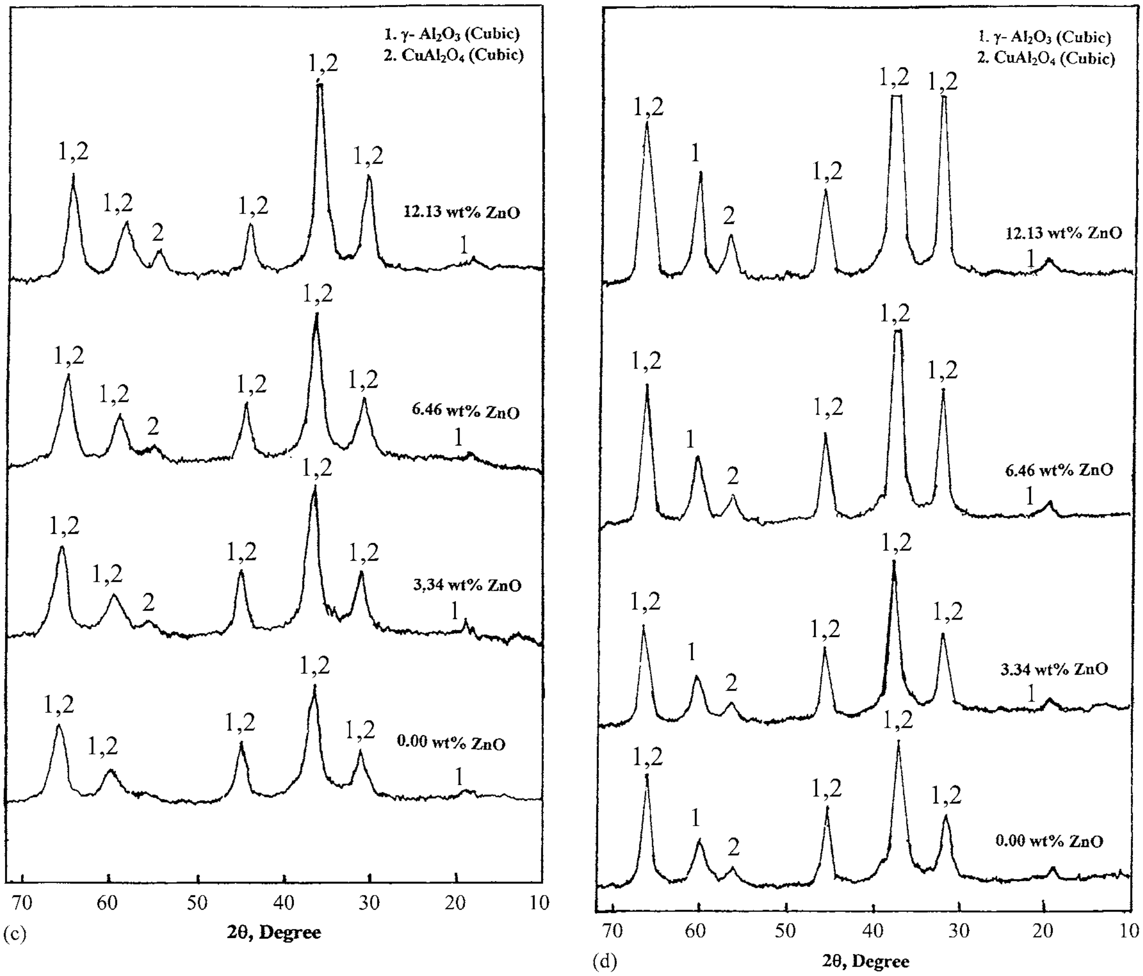

Fig. 2. (a) WAX diffraction of pure solid doped with different proportions of ZnO and preheated at 400 °C. (b) WAX diffraction of pure solid doped with different proportions of ZnO and preheated at 600 °C. (c) WAX diffraction of pure solid doped with different proportions of ZnO and preheated at 800 °C. (d) WAX diffraction of pure solid doped with different proportions of ZnO and preheated at 1000 °C.

proportions of ZnO. It seems that some of ZnO added dissolved in the matrices of $CuAl_2O_4$ phase forming solid solutions of formula $(Zn_xCu_{1-x})Al_2O_4$.

3.5. XRD investigation of the solid treated with MoO_3 and fired between 400 and 1000 °C

The solid treated with different proportions of MoO_3 and thermally treated at 400 and 600 °C are amorphous (not shown here). Furthermore, the XRD patterns of the solid treated with 2.96–19.63 wt.% MoO_3 and preheated at 800 and 1000 °C are shown in Fig. 3(a) and (b). It can be seen that the WAXD of the solids preheated to 800 °C showed the crystalline $CuAl_2O_4$ phase as well as γ-Al_2O_3.

A slight decrease in the line intensities of the copper aluminate phase was observed for solid doped with 2.96 wt.% MoO_3 and preheated at 800 °C, a significant decrease in line intensities was observed with increasing concentration of MoO_3 up to 19.63 wt.%. This is due to the formation of a copper molybdate phase according to the following equation:

$$CuO + MoO_3 \rightarrow CuMoO_4$$

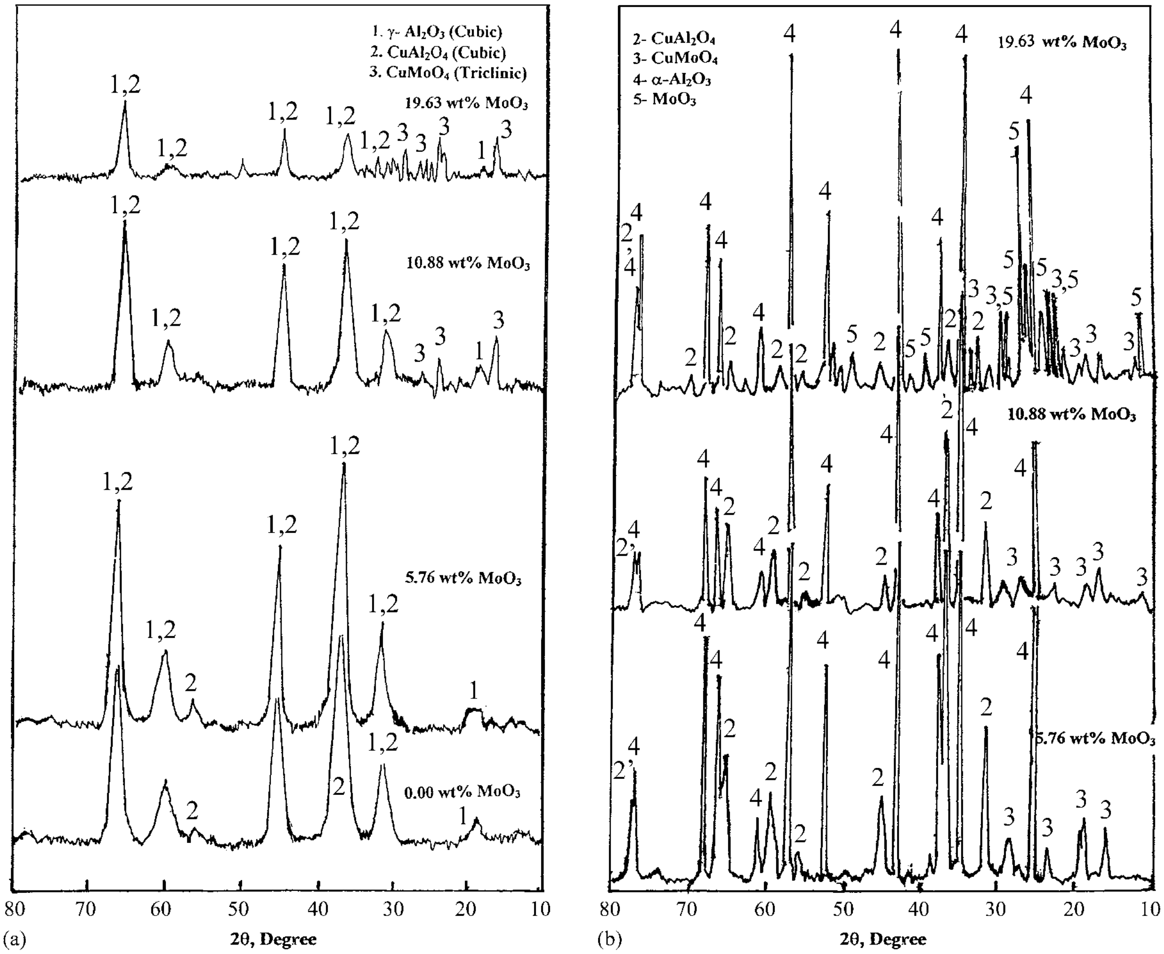

Fig. 3. (a) WAX diffraction of pure solid doped with different proportions of MoO_3 and preheated at 800 °C. (b) WAX diffraction of pure solid doped with different proportions of MoO_3 and preheated at 1000 °C.

The degree of crystallinity of the $CuMoO_4$ phase progressively increased with increasing in concentration of MoO_3 and also with increasing temperature from 800 to 1000 °C. From the above results, it seems that MoO_3 hinders the formation of copper aluminate phase, especially when it is present in high concentrations. This means that the treatment with MoO_3 has an opposite effect to that of ZnO treatment on the formation of crystalline copper aluminate phase at 800 and 1000 °C.

Furthermore, It is well known that the transformation of pure Al_2O_3 into α-Al_2O_3 (corundum) requires thermal treatment at temperature more than 1200 °C [23]. However, the WAXD of the solids treated with 5.76–19.63 wt.% MoO_3 and preheated at 1000 °C showed the formation of crystalline α-Al_2O_3 phase. This means that MoO_3 dissolved in the matrix of alumina and enhanced the crystallization process of γ-Al_2O_3 to α-Al_2O_3. This behavior has been observed in the case of Al_2O_3 treated with V_2O_5, and MoO_3 [21,24], but this was not observed in the case of solid treated with different portions of ZnO and preheated at 1000 °C. In this case, ZnO did not enhance the crystallization of γ-Al_2O_3 to α-Al_2O_3. This may be due to the formation of solid solution with formula $(Zn_xCu_{1-x})Al_2O_4$ and/or covering of the alumina surface with ZnO film acting as an energy barrier to stop the crystallization process of α-Al_2O_3 phase [12].

Furthermore, the WAXD of the solid treated with 19.63 wt.% MoO_3 and precalcined at 1000 °C showed diffraction lines relative to free MoO_3 (orthorhombic) phase. The detection of MoO_3 phase at this high temperature reflected the role of copper oxide and/or alumina plays as a stabilizer for MoO_3 phase and also for increasing its thermal stability.

3.6. Catalytic decomposition of H_2O_2 over pure and treated mixed solids thermally treated at 400–1000 °C

Preliminary experiments showed that MoO_3, ZnO and Al_2O_3 all obtained by the thermal treatment of their individual salts in air at 400, 600, 800 and 1000 °C exhibited no catalytic activity to decompose H_2O_2. On the other hand, CuO obtained by calcination of its salt at the same temperatures showed small catalytic activity. In general, the results obtained revealed that the reaction followed first-order kinetics [7] for all samples under investigation. Furthermore, it was found that the catalytic activity progressively increased with increasing the reaction temperature from 30 to 50 °C (see Fig. 4(a)).

3.7. Catalytic activity of pure CuO/Al_2O_3 system

Table 1 illustrates that the catalytic activity of CuO/Al_2O_3 system obtained at 400 and 600 °C was higher than that of CuO obtained at the same calcination temperatures. In this case, alumina oxide is a catalyst support [16] and prevents the aggregation of copper oxide to form crystalline CuO phase. In other words, alumina oxide increased the degree of dispersion of catalytically active constituents of CuO leading to increased surface area and consequently increased the catalytic activity. Fig. 4(a) shows that the catalytic activity of the mixed solid progressively decreased with increasing temperature up to 800 °C because of the formation of spinel copper aluminate phase. This phase restricts the catalytically active sites of the copper species in the tetrahedron position and consequently decreases catalytic activity [7].

3.8. Effect of MoO_3 treatment on catalytic behavior of CuO/Al_2O_3 system

Fig. 4(b) and Table 1 show the catalytic behavior of $0.20CuO/Al_2O_3$ system treated with 2.96–19.63 wt.%

Table 1
Effect of dopant concentration on the reaction rate constant (k), activation energy (ΔE) and Arrhenius factor ($\ln A$) for H_2O_2 decomposition conducted over pure Cu–Al mixed solids and those treated with MoO_3 and preheated at 400, 600 and 800 °C

MoO_3 added (wt.%)	Calcination temperature (°C)	k/10 min			ΔE (kJ/mol)	$\ln A$ (min^{-1})
		30 °C	40 °C	50 °C		
0.00	400	1.05	1.54	2.20	31	25.56
2.96		2.42	3.50	5.14	31	26.37
5.76		2.70	4.30	6.00	33	28.33
10.88		3.65	5.20	7.59	33	25.89
19.63		1.88	2.44	3.20	22	18.06
$CuNO_3$		0.2	0.40	0.70	42	33.93
0.00	600	0.85	1.34	2.05	38	31.60
2.96		1.73	3.18	4.40	39	33.35
5.76		2.30	3.60	5.89	39	33.49
10.88		1.20	2.04	3.43	43	36.46
19.63		0.65	1.20	2.19	50	42.15
$CuNO_3$		0.05	0.13	0.47	93	33.83
0.00	800	0.40	0.63	1.00	38	30.86
2.96		0.25	0.41	0.66	40	32.17
5.76		0.20	0.33	0.57	42	33.74
10.88		0.50	0.80	1.25	38	31.09
19.63		1.50	2.08	3.00	29	24.09
$CuNO_3$		0.023	0.07	0.25	99	82.60

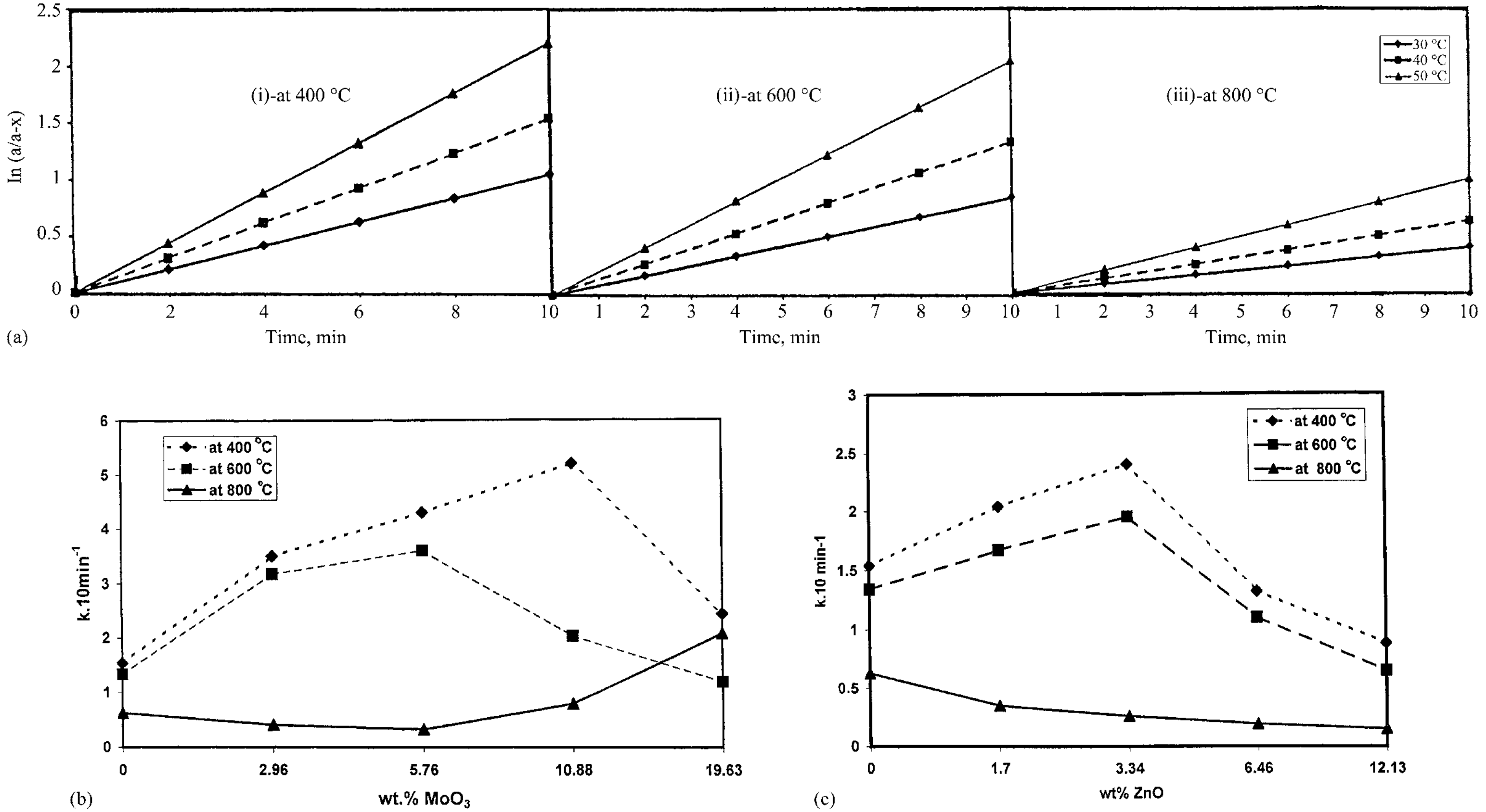

Fig. 4. (a) Dependence of ln(*a*/*a* – *x*) vs. time for pure Cu–Al mixed solid precalcined at 400 °C—(i); 600 °C—(ii) and 800 °C—(iii) at reaction temperatures 30, 40 and 50 °C. (b) Effect of MoO_3 treatment on catalytic behavior of $0.2CuO/Al_2O_3$ system at calcination temperatures, 400, 600 and 800 °C and at reaction temperature 40 °C. (c) Effect of ZnO treatment on catalytic behavior of $0.2CuO/Al_2O_3$ system at calcination temperatures, 400, 600 and 800 °C and at reaction temperature 40 °C.

Table 2
Effect of dopant concentration on reaction rate constant (k), activation energy (ΔE) and Arrhenius factor ($\ln A$) for H_2O_2 decomposition conducted over pure Cu–Al mixed solids and those treated with ZnO and preheated at 400, 600 and 800 °C

ZnO added (wt.%)	Calcination temperature (°C)	k/10 min			ΔE (kJ/mol)	$\ln A$ (min^{-1})
		30 °C	40 °C	50 °C		
0.00	400	1.05	1.54	2.20	31	25.56
1.70		1.40	2.04	2.85	29	24.04
3.34		1.55	2.40	3.20	30	25.10
6.46		0.93	1.32	1.91	30	24.09
12.13		0.48	0.88	1.32	42	34.71
$CuNO_3$		0.25	0.40	0.70	42	33.92
0.00	600	0.85	1.34	2.05	36	31.60
1.70		1.16	1.67	2.30	28	22.96
3.34		1.44	1.95	2.60	24	19.60
6.46		0.77	1.10	1.60	30	24.32
12.13		0.26	0.65	1.08	59	49.45
$CuNO_3$		0.05	0.13	0.47	93	33.83
0.00	800	0.40	0.63	1.00	38	30.86
1.70		0.20	0.35	0.60	46	24.07
3.34		0.15	0.26	0.48	48	38.80
6.46		0.13	0.19	0.35	41	32.77
12.13		0.08	0.15	0.28	52	41.80
$CuNO_3$		0.023	0.070	0.25	99	82.60

of MoO_3 and preheated at 400, 600 and 800 °C. It is seen that the catalytic activity of the solid treated with molybdenum oxide and preheated at 400 and 600 °C progressively increased with increasing the amount of MoO_3 up to certain extent. It reaches a maximum at 10.88 wt.% of MoO_3 for that preheated to 400 °C while it reaches a maximum with 5.76 wt.% of MoO_3 and preheated to 600 °C. Further increase in the amount of MoO_3 above this limit was followed by a significant decrease in the catalytic activity falling to values greater than that measured for the pure solids preheated at the same temperatures. The observed increase in the catalytic activity of pure solid due to treatment with MoO_3 reflects an effective increase in the concentration of catalytically active constituents of copper species and/or creation of new catalytic centers; Cu^{2+}–Mo^{5+}or Cu^{+}–Mo^{6+}; as a result of mutual charge interactions [25–27].

Furthermore, the WAXD patterns of the treated mixed solids preheated at 400 and 600 °C showed a progressive decrease in the degree of crystallinity. This reflects the decrease in the particle size, increasing surface area and consequently increasing catalytic activity. However, the greater the amount of MoO_3 added the greater the portion of the catalyst surface blocked with inactive species of molybdate. In other words, the high concentration of inactive MoO_3 on the catalyst surface led to a significant decrease in the concentration of catalytically active constituents and consequently a decrease in the catalytic activity of the system.

On the other hand, the catalytic activity of the solids treated with MoO_3 and preheated at 800 °C progressively decreased. However, it was noticed from Table 1 and Fig. 4(b) that the pure solid treated with 19.63 wt.% MoO_3 and preheated at 800 °C showed the highest catalytic activity of the solids preheated at the same temperature. This is attributed to the formation of an active $CuMoO_4$ compound [26].

3.9. Effect of ZnO treatment on catalytic behavior of CuO/Al$_2$O$_3$ system

Fig. 4(c) and Table 2 show that the catalytic activity of 0.20 CuO/Al_2O_3 system progressively increased with increasing ZnO doping. It reaches a maximum at 3.34 wt.% ZnO then decreases significantly in catalytic activity is for various solids precalcined at 400 and 600 °C. The X-ray results of the solid doped with ZnO and treated at the same temperatures explained the above results in that: ZnO treatment of the pure solid leads to a significant decrease in the diffraction intensity. This shows that there is a decrease in particle size with dispersion and consequently leading to an increase in catalytic activity. This means that up to 3.34 wt.% of ZnO doping of solid and preheated at 400 and 600 °C there is an increase in catalytically active constituents. However, further increase of dopant concentration up to 12.13 wt.% ZnO is followed by a significant decrease in the catalytic activity. In this case, excess of inactive ZnO might block most of the active sites in the CuO/Al_2O_3 system leading to a decrease in the catalytic activity of heavily doped solids. On the other hand, the activity progressively decrease with increasing treatment temperature of solid treated with ZnO from 600 to 800 °C because of the effect of ZnO in stimulating crystallization and formation of inactive $CuAl_2O_4$ phase at 800 °C as previously mentioned.

In general, all the solids treated at high temperature, especially at 1000 °C do not show any catalytic performance because of the sintering process of catalytically active sites and/or formation of inactive compounds such as $CuAl_2O_4$, $(Zn_xCu_{1-x})Al_2O_4$, MoO_3 or α-Al_2O_3 [7,16].

Finally, from the values of the rate constants (*k*/min) measured at 30, 40 and 50 °C over pure and variously treated solids preheated at 400, 600 and 800 °C have enabled ΔE to be calculated by direct application of the Arrhenius equation. The calculated values of ΔE are listed in Tables 1 and 2. In some cases, there is a discrepancy between the activation energies and catalytic activity so we calculated the pre-exponential (*A*) constant in the Arrhenius equation and these are listed in Tables 1 and 2.

Inspection of the data listed in Tables 1 and 2 show that: (a) for pure solids treated with 2.96–10.58 wt.% MoO_3 and those treated with 1.70–6.46 wt.% ZnO the activation energies values were clustered within the same ranges as follows: 31–33, 38–43 and 38–42 kJ/mol for pure solids treated with MoO_3 and 29–31, 24–36 and 38–48 kJ/mol for those solids treated with ZnO and preheated at 400, 600, and 800 °C, respectively. This reflects the presence of the same nature of catalytically active sites [12]. Furthermore, the observed increase in catalytic activity upon treatment of the solid with certain limits of MoO_3 or ZnO and calcined at 400 and 600 °C means that the role of MoO_3 and ZnO treatment is to increase the concentration of active constituents; (b) the solid treated with 19.63 wt.% MoO_3 and that treated with 12.13 wt.% ZnO preheated at 400, 600 and 800 °C shows changes in catalytic performance and activation energies to those treated with 2.96–10.58 wt.% MoO_3 and those treated with 1.70–6.46 wt.% ZnO and thermally treated at the same temperatures. This means the change in the nature of catalytically active constituents of the system by formation of new ion pairs as Cu^{2+}–Mo^{5+}or Cu^{+}–Mo^{6+} or formation active compound such as $CuMoO_4$ in case of increasing the catalytic activity or formation of inactive compounds [7] such as $CuAl_2O_4$, $(Zn_xCu_{1-x})Al_2O_4$, MoO_3 and α-Al_2O_3 in case of decreasing catalytic activity.

4. Conclusions

The main conclusions that may be drawn from the results are:

1. γ-Al_2O_3 phase is detected for all solids preheated at 400 and 600 °C, while no diffraction lines relative to CuO phase are detected at different treatment temperatures.
2. Crystalline $CuAl_2O_4$ phase is formed as a result of solid–solid interaction between CuO and Al_2O_3 at 800 °C. The line intensities and the particle size of copper aluminate phase progressively increased with increasing treatment temperature of pure solid from 800 to 1000 °C.
3. ZnO treatment enhanced the formation and crystallization of $CuAl_2O_4$ phase and it may form solid solutions of formula $(Zn_xCu_{1-x})Al_2O_4$. Furthermore, no diffraction lines relative to ZnO or $ZnAl_2O_4$ phases were detected for solid treated with ZnO and preheated at 400–1000 °C.
4. MoO_3 treatment hindered the formation and crystallization of $CuAl_2O_4$ phase at 800 and 1000 °C because of the formation of crystalline copper molybdate phase.
5. MoO_3 treatment enhanced the crystallization process of γ-Al_2O_3 into α-Al_2O_3 at 1000 °C while ZnO treatment has no effect.

6. MoO_3 treatment enhanced the catalytic activity of pure solid preheated at 400–800 °C up to certain extent of treatment. This behavior is attributed to increase in the concentration of catalytically active constituents of copper species and/or creation of new catalytic centers; Cu^{2+}–Mo^{5+}or Cu^{+}–Mo^{6+}, as a result of mutual charge interactions.
7. The catalytic activity of pure solid treated with ZnO and preheated at 400 and 600 °C progressively increased up to 3.34 wt.% ZnO then it progressively decreased with increasing of ZnO concentration up to 12.13% and also with increasing treatment temperature to 800 °C.
8. No catalytic activity noticed for all solids thermally treated at 1000 °C because of sintering process of catalytically active sites and/or formation of inactive phases such as $CuAl_2O_4$, MoO_3, $(Zn_xCu_{1-x})Al_2O_4$ and α-Al_2O_3.

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