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Effects of Li_2O doping on surface and catalytic properties of $\text{CuO-ZnO/Al}_2\text{O}_3$ system

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Abstract

The effect of Li_2O doping (0.375–4.5 mol.%) on surface and catalytic properties of $\text{CuO-ZnO/Al}_2\text{O}_3$ was investigated using nitrogen adsorption at -196°C and catalytic oxidation of CO by O_2 at $150\text{--}200^\circ\text{C}$. Pure and doped solids were subjected to thermal treatment at $600\text{--}800^\circ\text{C}$ prior to surface and catalytic measurements.

The results showed that Li_2O doping caused measurable increases in the specific surface area (23–45%) and in the total pore volume (24–43%) for the adsorbents preheated in air at $600\text{--}700^\circ\text{C}$. If the doping process was carried out at 600°C , it resulted in a considerable decrease (52%) in the catalytic activity, measured at 175°C . A rise in calcination temperature of the doped solid specimens (4.5 mol.% Li_2O) to 700 and 800°C brought about marked increases of 125% and 186%, respectively, in the catalytic activity measured at 175°C . This discrepancy is discussed in terms of the effect of Li_2O doping in decreasing the dispersity of CuO crystallites of the solids calcined at 600°C and the role of Li_2O in hindering CuAl_2O_4 formation upon calcination at 700 and 800°C . The decrease in the degree of dispersion of CuO crystallites due to doping at 600°C is normally followed by a decrease in the catalytic activity while the suppression or hindrance of CuAl_2O_4 formation might be followed by an increase in the catalytic activity. The doping process carried out at $600\text{--}800^\circ\text{C}$ did not modify the concentration of catalytically active constituents involved in chemisorption and catalysis of the CO oxidation reaction. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Surface properties; Catalytic properties; $\text{CuO-ZnO/Al}_2\text{O}_3$ system; Li_2O doping

1. Introduction

It is well known that the activity and selectivity of a large variety of catalysts can be modified by various methods such as loading on a finely divided support [1–6], subjecting them to ionizing radiations [7–15] and doping with certain foreign oxides [16–21]. The loading on a suitable support material results in an increase in the dispersity of catalytically active constituents [1–6] and increases their thermal stability via hindering their grain

growth. However, metal–support interactions may take place during the operation of supported catalysts and cause a decrease in the catalytic activity of these catalysts owing to the formation of a metal oxide–support compound which is characterized by an activity lower than that of the metal oxide itself. In the case of the $\text{CuO/Al}_2\text{O}_3$ system, ZnO is added to suppress the solid–solid interaction between copper and aluminium oxides to produce the compound CuAl_2O_4 [22, 23]. Ionizing radiation may modify the texture characteristics and the chemistry of the catalyst's surface, e.g. its acidity, its oxidation character and its semicon-

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ducting properties [1–15]. The changes in these characteristics may be accompanied by changes in the catalytic activity and selectivity of the treated catalysts [2,3,7,8,13–15]. Doping of catalysts with certain oxides may alter their surface electrical and catalytic properties.

The present investigation reports a study on the effect of Li_2O doping on metal–support interactions, surface and catalytic properties of $\text{CuO–ZnO/Al}_2\text{O}_3$ system using X-ray diffraction (XRD), nitrogen adsorption at -196°C and catalysis of CO oxidation by O_2 at $150\text{–}200^\circ\text{C}$.

2. Experimental details

2.1. Materials

A $\text{CuO–ZnO/Al}_2\text{O}_3$ mixed solids sample was prepared by treating a known mass of a finely powdered Al(OH)_3 with a solution containing a calculated amount of zinc nitrate. The paste obtained was dried at 100°C then calcined in air at 500°C for 5 h. The calcined solid was impregnated with copper nitrate solution, dried at 100°C then heated in air at 600, 700 and 800°C for 5 h. The nominal composition of the calcined solids sample was 0.25 CuO , 0.06 $\text{ZnO/Al}_2\text{O}_3$. The doped mixed solids were prepared by treating Al(OH)_3 with LiNO_3 solution, drying at 100°C then treating with $\text{Zn(NO}_3)_2$ solution followed by impregnation with $\text{Cu(NO}_3)_2$ solution, the obtained solids were dried at 100°C then calcined in air at 600, 700 and 800°C for 5 h. The amounts of dopant were 0.375, 0.75, 1.5, 3 and 6 mol.% Li_2O . The employed Al(OH)_3 solid was obtained by precipitation from aluminium nitrate solution using 0.2 M NH_4OH at 70°C and $\text{pH}=8$, the precipitate was washed with distilled water and dried at 100°C till constant weight. The chemicals employed were of analytical grade and supplied by Prolabo company.

2.2. Techniques

X-ray diffractograms of pure and doped solids preheated in air at $600\text{–}800^\circ\text{C}$ were obtained using a Philips diffractometer (type PW 13890). The

patterns were run with nickel-filtered copper radiation ($\lambda = 1.5405 \text{ \AA}$) at 36 kV and 16 mA with scanning speed of 2° in $2\theta \text{ min}^{-1}$.

The surface characteristic namely S_{BET} , V_p and r of pure and doped solids were determined from N_2 adsorption isotherms conducted at -196°C using a conventional volumetric apparatus. Before carrying out the measurements, each sample was degassed under a reduced pressure of 10^{-5} Torr at 200°C for 3 h.

The catalytic oxidation of CO by O_2 was carried out on various catalysts at temperatures between 150 and 200°C using a static method. A fresh 200 mg catalyst sample was employed for each kinetic experiment and was activated by heating at 300°C for 2 h. under a reduced pressure of 10^{-6} Torr. The kinetics of the catalysed reaction were monitored by measuring the pressure of the reaction mixture at different time intervals until equilibrium was attained. The reaction product (CO_2) was removed from the reaction atmosphere by freezing in a liquid nitrogen trap so the percentage decrease in the pressure of the reacting gases at a given time interval gives the percentage conversion of the catalytic reaction at that time.

3. Results and discussion

3.1. XRD of calcination products of pure and doped mixed solids

X-ray diffractograms of pure and doped mixed solids preheated in air at 600 and 800°C were taken. Figs. 1 and 2 show the diffractograms of pure and doped mixed solids precalcined at 600 and 800°C . Fig. 1 reveals that pure mixed solids heated at 600°C consists of a poorly crystalline CuO phase and its degree of crystallinity increases on increasing the dopant concentration. The height of the main diffraction line of the CuO phase was 3, 7, 12 and 24 (arbitrary units) for the pure oxide sample and for samples treated with 0.75, 1.5 and 4.5 mol.% Li_2O and calcined at 600°C , respectively. This finding shows that Li_2O doping increases the degree of crystallinity of the CuO phase to an extent proportional to the amount of Li_2O added. Similar results have been reported in

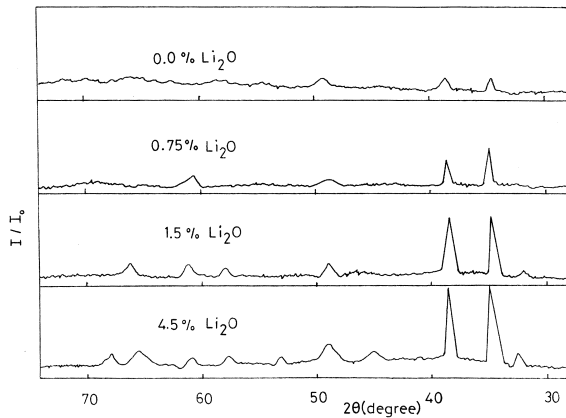


Fig. 1. X-ray diffractograms of pure and doped CuO–ZnO/ Al_2O_3 solids calcined at 600°C.

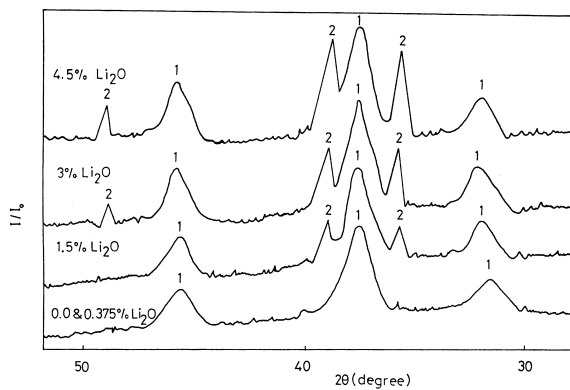


Fig. 2. XRD patterns of pure and doped solids precalcined at 800°C: (1) CuAl_2O_4 phase; (2) CuO phase.

our recent investigation [24] of CuO–ZnO/ Al_2O_3 doped with Na_2O and also heated at 600°C. The ordering of CuO crystallites due to doping may be reflected as a decrease in the dispersity of copper oxide phase. So, the doping process may lead to a decrease in the degree of dispersion of CuO present in the mixed solids specimens. It is known that an Al_2O_3 support has the ability to disperse transition metal oxides on its surface. This ability is defined as monolayer dispersion capacity [25]. This term expresses the amount of a given metal oxide to be dispersed on the alumina surface and to cover it with a layer one molecule in thickness and is given as the mass of transition metal oxide per 100 m^2 of the alumina surface [26,27]. It seems that added

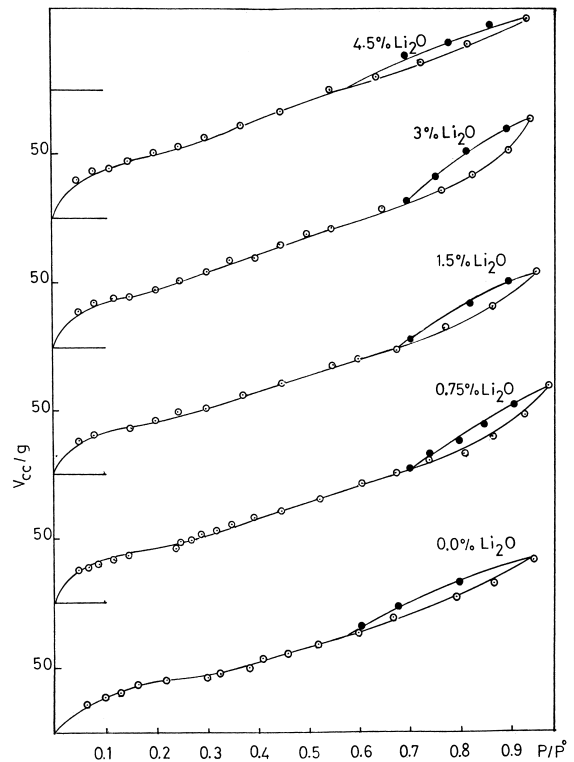


Fig. 3. N_2 adsorption isotherms for pure and doped adsorbents precalcined at 700°C.

lithium oxide is retained on the alumina surface and hinders the uptake of CuO on its surface, leading to aggregation or crystallization of CuO crystallites into a well-ordered CuO phase.

Fig. 2 shows that pure mixed solids and those treated with 0.375 mol.% Li_2O and calcined at 800°C were converted entirely into a copper aluminate compound having a reasonable degree of crystallinity. On the other hand, the mixed oxide samples treated with $\text{Li}_2\text{O} > 0.375$ mol.% and heated at 800°C consist of a mixture of unreacted CuO and CuAl_2O_4 phases and the magnitude of all the diffraction lines of CuO phase increases progressively with increasing the amount of dopant added. These results suggest that Li_2O doping followed by calcination at 800°C hinders the solid–solid interactions between CuO and Al_2O_3 producing CuAl_2O_4 phase. Added Li_2O may cover the surfaces of Al_2O_3 particles hindering the diffusion of CuO towards the interior of Al_2O_3 grains.

Table 1
Surface characteristics of pure and doped adsorbents precalcined at different temperatures

Li ₂ O (mol.%)	Calcination temperature (°C)	S _{BET} (m ² g ⁻¹)	S _t (m ² g ⁻¹)	V _p (cm ² g ⁻¹)	r (Å)	BET-C
0.00	600	175	168	0.198	23	33
0.75		178	200	0.244	34	62
1.50		198	196	0.209	21	49
3.00		210	204	0.263	25	53
4.50		216	220	0.285	26	81
0.00	700	141	150	0.208	37	21
0.75		157	175	0.257	41	28
1.50		180	175	0.235	33	31
3.00		190	206	0.272	36	29
4.50		204	200	0.226	28	36
0.00	800	127	137	0.164	32	13
0.75		145	144	0.176	30	10
1.50		147	156	0.206	35	11
3.00		150	153	0.176	28	11
4.50		158	150	0.179	28	11

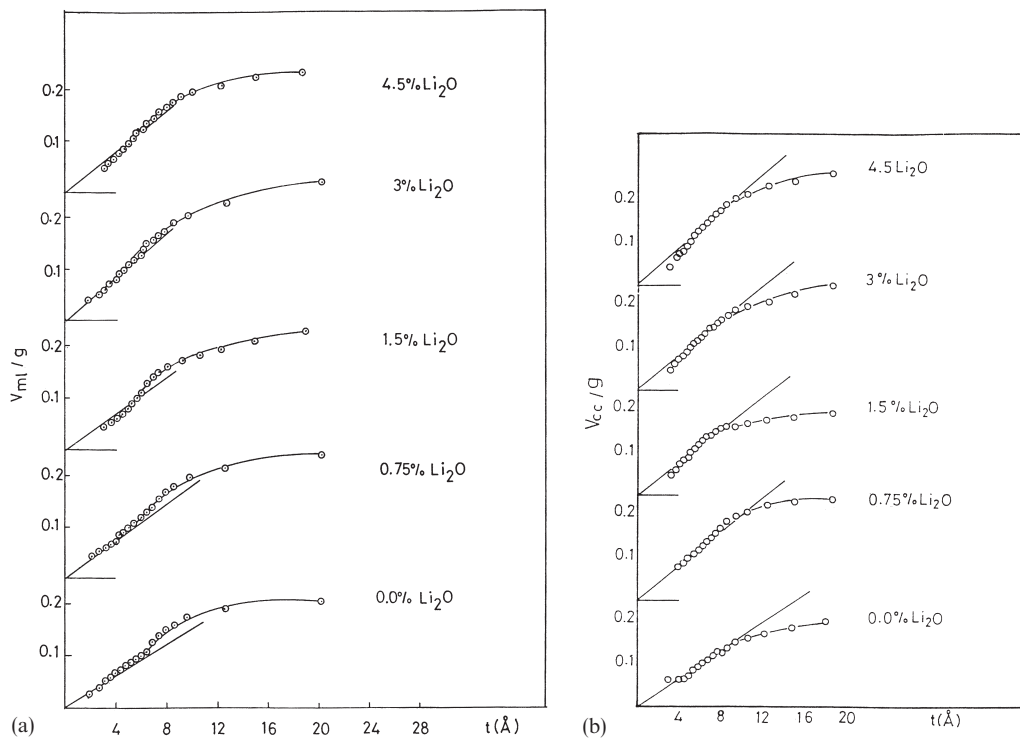


Fig. 4. (a) $V_{i,t}$ plots for pure and doped adsorbents precalcined at 700°C. (b) Volume thickness plots for pure and doped adsorbents precalcined at 600°C.

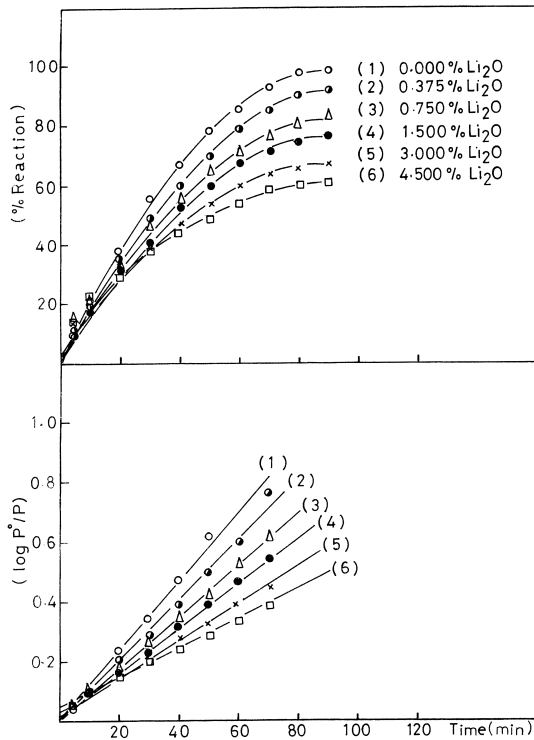


Fig. 5. Kinetic curves and first-order plots of CO oxidation by O_2 conducted at $175^\circ C$ over pure and doped catalysts heated at $600^\circ C$.

Hence, the Li_2O film formed acts as an energy barrier to the diffusion of copper species in the bulk of Al_2O_3 .

3.2. Effect of Li_2O doping on surface properties of various mixed solids

The different surface characteristics of pure and doped $CuO-ZnO/Al_2O_3$ solids preheated at 600, 700 and $800^\circ C$ were determined from nitrogen adsorption isotherms conducted at $-196^\circ C$. These characteristics include specific surface area (S_{BET}), total pore volume (V_p) and mean pore radius (r). The adsorption isotherms obtained belong to type II of the Brunauer classification [28] and representative isotherms are given in Fig. 3. The S_{BET} values for pure and doped adsorbent were computed from linear plots of the BET equation. The data obtained are given in Table 1 which includes also the values of V_p and r [29].

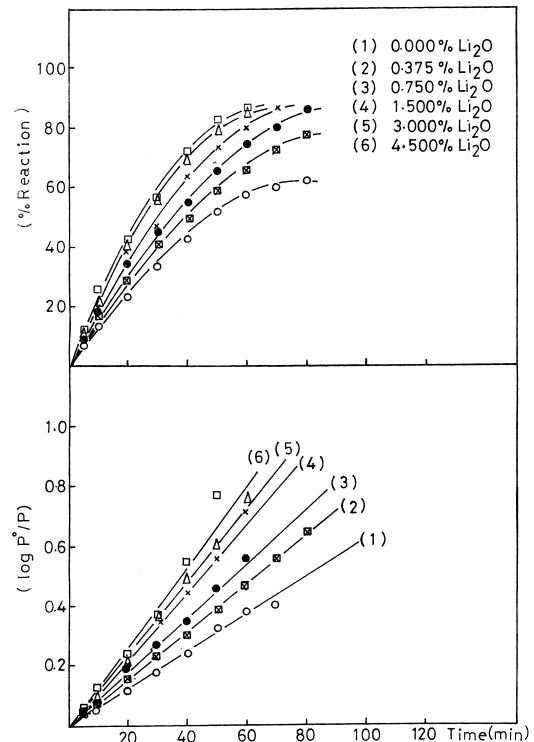


Fig. 6. Kinetic curves and first-order plots of CO oxidation by O_2 over pure and doped catalysts heated at $700^\circ C$.

An additional set of specific surface areas S_t was obtained from volume–thickness curves (V_{t-t} plots). The V_{t-t} plots obtained are similar for pure and doped solids calcined at the same temperature. Fig. 4(a) shows the V_{t-t} plots of pure and doped solids preheated at $700^\circ C$. These plots were constructed using suitable standard t curves depending on the magnitude of the constant C in the BET equation. It is seen from Fig. 4(a) and (b) that pure and doped solids precalcined at $600^\circ C$ consist mainly of narrow pores and those treated at $700^\circ C$ contain mainly wide pores as indicated from downward and upward deviation of their V_{t-t} plots. The plots of pure and doped mixed solids heated at $800^\circ C$ (not shown) show the presence of wide pores as dominant porosity. The different computed surface characteristics of pure and doped solid specimens preheated at 600, 700 and $800^\circ C$ are given in Table 1. Inspection of the results included in Table 1 revealed the following. (i) The values of S_{BET} and S_t are close to each other for

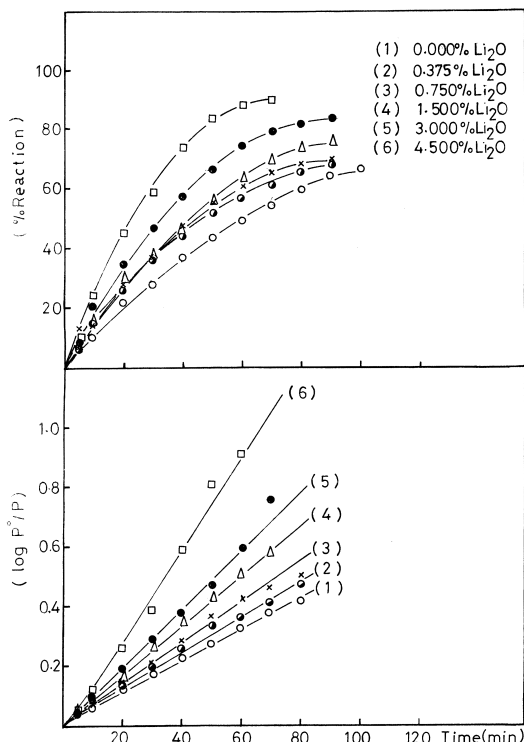


Fig. 7. Kinetic curves and first-order plots of CO oxidation by O₂ conducted at 175°C over pure and doped solids heated at 800°C.

the different investigated adsorbents which justifies the correct choice of standard t curves for pore analysis and indicates the absence of ultramicro pores in these adsorbents. (ii) Li₂O doping resulted in a progressive increase in the S_{BET} and V_p for the solids calcined at 600–800°C. (iii) The maximum increase in the specific surface area and total pore volume are 23 and 43% for the solids heated at 600°C, 45 and 31% for the adsorbents calcined at 700°C and 24 and 26% for the mixed solids preheated 800°C.

The increase induced in the S_{BET} and V_p values for the CuO–ZnO/Al₂O₃ system as a result of doping with Li₂O followed by heating at 600–800°C can be attributed to the creation of pores produced from liberation of gaseous nitrogen oxides during the thermal decomposition of LiNO₃ from the thermal treatment of doped mixed solids at 600–800°C. Similar results have been

reported in the case of CuO/Al₂O₃ and NiO/Fe₂O₃ systems [20,21].

3.3. Catalytic oxidation of CO by O₂ on pure and doped solids

The catalytic oxidation of CO by O₂ over pure and doped mixed solids precalcined at 600, 700 and 800°C was conducted at 150–200°C. The results showed that the catalysis of CO oxidation by O₂ follows first-order kinetics over pure and doped catalyst samples.

Fig. 5 shows kinetic curves and first-order plots for the catalytic reaction conducted at 175°C over pure and doped solids preheated at 600°C. The slope of the first-order plots determines the magnitude of the reaction rate constant (k) of the catalysed reaction carried out at a given temperature. It is seen from Fig. 5 that k decreases progressively on increasing the dopant concentration, and the maximum decrease due to doping with 4.5 mol.% Li₂O was 52%. The doping of CuO–ZnO/Al₂O₃ mixed solids at 600°C resulted in an increase in the specific surface area (23%) of the treated solids. This increase in S_{BET} is expected to be followed by an increase and not a decrease in the catalytic activity. It seems that a parameter other than the specific surface area determines the catalytic activity. The CuO phase represents the catalytically active constituents of the solids investigated. It is seen from Fig. 1 that Li₂O doping at 600°C resulted in an increase in the degree of ordering of the CuO phase. This increase may reflect an induced decrease in the dispersity of copper oxides phase via an enhanced crystallization of CuO crystallites leading to a corresponding decrease in the concentration of CuO on the outermost surface layers of the treated solids.

Figs. 6 and 7 represent kinetic curves and first-order plots of the catalytic reaction conduction at 175°C over different pure and doped solids preheated at 700 and 800°C. It is observed from Figs. 6 and 7 that the catalytic activity measured at 175°C, for the various investigated solids calcined at 700 and 800°C increases progressively as a function of the dopant concentration. The maximum increase in the catalytic activity due to doping at 700 and 800°C reached 122 and 186%,

Table 2
Activation energy and frequency factor for the catalytic oxidation of CO by O₂ over pure and doped solids

Li ₂ O (mol.%)	Calcination temperature (°C)	ΔE (kJ mol ⁻¹)	log <i>A</i>	ΔE^* (kJ mol ⁻¹)
0.00	600	15.9	-0.110	15.9
0.375		14.0	-0.397	16.5
0.75		12.1	-0.647	16.7
1.50		12.2	-0.719	16.4
3.00		15.9	-0.307	17.6
4.50		15.3	-0.426	18.0
0.00	700	15.9	-0.387	15.9
0.375		19.1	0.114	14.8
0.75		19.1	0.164	14.3
1.50		20.4	0.412	13.6
3.00		19.1	0.284	13.3
4.50		17.2	0.108	12.9
0.00	800	35.7	1.839	35.7
0.75		35.7	1.882	35.7
1.50		48.4	3.421	34.7
3.00		44.6	3.071	34.0
4.50		38.2	2.349	34.0

respectively. The observed increase in the specific surface area of CuO–ZnO/Al₂O₃ system due to Li₂O doping at 700 and 800°C (45 and 24%) did not account for the observed important increase in their catalytic activities. The hindrance of CuAl₂O₄ formation due to Li₂O doping at 800°C (see Fig. 2) can be considered as the major reason for the induced increase in the activities of the doped solids. In fact CuAl₂O₄ is characterized by a catalytic activity, in oxidation–reduction reactions, lower than that of CuO [22]. The conversion of CuO into CuAl₂O₄ is normally accompanied by a decrease in the catalytic activity of the treated solids.

The doping of various investigated solids preheated at 600–800°C may change the mechanism of the catalysed reaction besides changing their catalytic activities. This can be verified via the determination of the activation energy of the catalytic reaction (ΔE) conducted over pure and doped solids.

3.4. Effect of Li₂O doping on ΔE of the catalysed reaction

The values of *k* measured at different temperatures (150–200°C) in contact with pure and

treated catalysts precalcined at 600–800°C enables ΔE to be determined by direct application of the Arrhenius equation. The computed values of ΔE for the various catalysts investigated are listed in Table 2. Also included in Table 2 are the values of log *A* (frequency factor in the Arrhenius equation) calculated for pure and doped solids. It is observed from the results given in Table 2 that Li₂O doping carried out at 600–800°C brought about a fluctuation in ΔE values, i.e. both increases and decreases were found. However, the increase in the value of ΔE was accompanied by a corresponding increase in the value of log *A* and vice versa. Hence, the observed change in ΔE value due to Li₂O doping of CuO–ZnO/Al₂O₃ solids may result from the change in the magnitude of the frequency factor. In fact, the activation energy of the catalytic reaction over different pure and doped catalysts was recalculated with the values of *A* for pure solids calcined at 600, 700 and 800°C being adopted for the doped catalysts heated at the same temperatures, i.e. log *A* values of -0.11, 0.39 and 1.89 found for pure solids calcined at 600, 700 and 800°C, respectively were adopted for the different doped solids calcined at the same temperatures. The recalculated values of the activation energy

ΔE^* for the various solids investigated are listed in the last column of Table 2. The comparison of ΔE^* for pure and doped catalysts revealed that Li_2O doping did not much modify the activation energy of CO oxidation reaction by O_2 over different solids: ΔE^* values of 17 ± 1 , 14 ± 1 and 35 ± 1 kJ mol^{-1} were found for pure and doped $\text{CuO-ZnO/Al}_2\text{O}_3$ solids calcined at 600, 700 and 800°C, respectively. These results clearly indicate that Li_2O doping of $\text{CuO-ZnO/Al}_2\text{O}_3$ solids at 600, 700 and 800°C did not modify the mechanism of the catalysed reaction but changed the concentration of catalytically active constituents without altering their energetic nature.

4. Conclusions

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

(1) Li_2O doping (0.375–4.5 mol.%) of $\text{CuO-ZnO/Al}_2\text{O}_3$ at 600°C enhances the crystallization of the CuO phase to an extent proportional to its amount, owing to a decrease in the monolayer dispersion capacity of Al_2O_3 towards CuO phase. The doping process conducted at 800°C hinders the solid–solid interactions yielding CuAl_2O_4 owing to coating of the surfaces of Al_2O_3 particles with a film of Li_2O that opposes the diffusion of copper species through the outermost surface layers of Al_2O_3 towards its bulk.

(2) A progressive increase occurs in the S_{BET} and V_p values of the treated adsorbents (23–45% and 24–43%) owing to creation of new pores during the liberation of gaseous nitrogen oxides resulting from the thermal decomposition of LiNO_3 .

(3) The catalytic activity in CO oxidation by O_2 at 150–200°C over pure and doped solids was found to decrease as a function of the dopant concentration for the solids calcined at 600°C and to increase monotonically for the catalysts preheated at 700 and 800°C. The decrease in the catalytic activity due to doping at 600°C is directly related to a decrease in the dispersity of CuO crystallites which act as the catalytically active constituents. The observed increase in the catalytic activity due to Li_2O doping conducted at 700,

800°C was attributed mainly to a hindrance of CuAl_2O_4 formation.

(4) Li_2O doping at 600–800°C did not modify the mechanism of CO oxidation by O_2 but modified the concentration of catalytically active components without changing their energetic nature.

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