

Effect of Li_2O and CoO -doping of $\text{CuO}/\text{Fe}_2\text{O}_3$ system on its surface and catalytic properties

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Abstract

Physicochemical, surface and catalytic properties of pure and doped $\text{CuO}/\text{Fe}_2\text{O}_3$ system were investigated using X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX), nitrogen adsorption at -196°C and CO -oxidation by O_2 at 80 – 220°C using a static method. The dopants were Li_2O (2.5 mol%) and CoO (2.5 and 5 mol%). The results revealed that the increase in precalcination temperature from 400 to 600°C and Li_2O -doping of $\text{CuO}/\text{Fe}_2\text{O}_3$ system enhanced CuFe_2O_4 formation. However, heating both pure and doped solids at 600°C did not lead to complete conversion of reacting oxides into CuFe_2O_4 . The promotion effect of Li_2O dopant was attributed to dissolution of some of dopant ions in the lattices of CuO and Fe_2O_3 with subsequent increase in the mobility of reacting cations. CoO -doping led also to the formation of mixed ferrite $\text{Co}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$. The doping process of the system investigated decreased to a large extent the crystallite size of unreacted portion of Fe_2O_3 in mixed solids calcined at 600°C . This process led to a significant increase in the S_{BET} of the treated solids. Doping $\text{CuO}/\text{Fe}_2\text{O}_3$ system with either Li_2O or CoO , followed by calcination at 400 and 600°C decreased its catalytic activity in CO -oxidation by O_2 . However, the activation energy of the catalyzed reaction was not much affected by doping.

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1. Introduction

Most of divalent metal oxides interact with Fe_2O_3 yielding the corresponding ferrite having the formula $M\text{Fe}_2\text{O}_4$. The physical properties of ferrites are related to the structure of these solids which have a spinel structure. The spinel-type ferrites are commonly utilized in fine electronic devices owing to their remarkable magnetic and semiconducting properties [1–5]. Unlike single oxides or their mixtures, the single phase spinel-type binary and ternary oxides show extra structural stability and exhibit interesting catalytic properties. The catalytic activity of spinels containing transition metal ions is influenced by the acid–base and redox properties of these ions, as well as by their distribution among the octahedral and tetrahedral sites in the spinel structure. It had been established that the octahedral sites are almost exclusively exposed at the surface of the spinel crystallites and that the catalytic activity is

mainly due to octahedral cations [6]. Ferrites have been used as catalysts for some industrially important reactions, such as oxidative dehydrogenation of butene to butadiene, hydrodesulphurisation of petroleum crude and the treatment of automobile exhaust gases [7].

Nanocrystalline ferrites can be obtained by a variety of methods. The choice of the appropriate method depends mainly upon the specific use of the produced ferrite. These methods as ball-milling [8,9], solid state reaction [10], co-precipitation [10,11] and combustion synthesis [12] have been applied for preparation of copper ferrite powders. It is not easy to get nanocrystalline oxides by solid state reaction because of the required high temperature, which results in the increase of particle size. Co-precipitation is a simple and effective method for the preparation of multicomponent oxides.

The magnetic, semiconducting and catalytic properties of the prepared ferrite depend, mainly on the method of preparation, chemical composition, calcination conditions, structure and surface properties of the Fe_2O_3 used and the addition of small amounts of certain foreign oxides [13,14]. The effects of doping

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with certain foreign oxides on the formation of a big variety of ferrites made the object of several investigations carried out by El-Shobaky et al [15–23]. These authors claimed that the formation of nickel, cobalt, manganese, magnesium and cadmium ferrites could be enhanced by doping with Li_2O or ZnO or Al_2O_3 . The degree of enhancement of ferrite formation depends on the nature of both the dopant and the transition metal oxide interacting with Fe_2O_3 .

The present work aimed to investigate the effect of calcination temperature and doping of $\text{CuO}/\text{Fe}_2\text{O}_3$ system with Li_2O and CoO on the formation of CuFe_2O_4 and its surface and catalytic properties. The techniques employed were X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX), nitrogen adsorption at -196°C and catalytic oxidation of CO by O_2 at $80\text{--}220^\circ\text{C}$.

2. Experimental

2.1. 2.1. Materials

Copper and iron mixed hydroxides sample were prepared by coprecipitation from an aqueous solution of copper and iron nitrates (Fe/Cu ratio = 2:1) using 6 M NaOH solution at 65°C and pH 10. The precipitate was carefully washed with distilled water, filtered then dried at 120°C till a constant weight, then calcined in air at 400 and 600°C for 6 h. The doped solid samples were obtained by treating a known weight of dried mixed hydroxides with calculated amounts of lithium or cobalt nitrates dissolved in least volume of distilled water sufficient to make pastes. The pastes were dried at 120°C , then calcined in air at 400 and 600°C for 6 h. The dopant concentrations were 2.5 mol% Li_2O , 2.5 and 5 mol% CoO . The chemicals employed were of analytical grade supplied by BDH company.

2.2. Techniques

X-ray powder diffractograms of pure and variously doped samples calcined in air at 400 and 600°C were determined

using a Bruker diffractogram (Bruker D8 advance target). The patterns were run with $\text{Cu K}\alpha_1$ with secondly monochromator ($\lambda = 1.5405 \text{ \AA}$) at 40 kV and 40 mA. The crystallite size of crystalline phases present in different solids investigated was calculated from line broadening of the main diffraction lines of CuO , $\alpha\text{-Fe}_2\text{O}_3$ or CuFe_2O_4 phases using Scherrer equation [24]

$$d = K\lambda / \beta_{1/2} \cos \theta$$

where d is the mean crystallite diameter, λ is the X-ray wave length, K is the Scherrer constant (0.89), $\beta_{1/2}$ is the full width at half maximum (FWHM) of the diffraction peaks of CuO , $\alpha\text{-Fe}_2\text{O}_3$ or CuFe_2O_4 and θ is the diffraction angle. The scanning rate was 8° and 0.2 in $2\theta/\text{min}$ in phases identification and line broadening profile analysis, respectively.

Energy dispersive X-ray analysis EDX measurements were carried out on a Hitachi S-800 electron microscope with a Kevex Delta system attached. The parameters were as follows: -15 kV accelerating voltage, 100 s accumulation time, $8 \mu\text{m}$ window width. The surface molar composition was determined by the Asa method (Zaf-correction, Gaussian approximation).

The specific surface areas (S_{BET}) of various solid catalysts were determined from nitrogen adsorption isotherms measured at -196°C using conventional volumetric apparatus. Before undertaking such measurements, each sample was degassed under a reduced pressure of 10^{-5} Torr for 2 h at 200°C .

The catalytic oxidation of CO by O_2 on different catalyst samples was conducted at $80\text{--}220^\circ\text{C}$ using a static method. A fresh 200 mg catalyst sample was employed in each kinetic experiment and was activated by heating at 300°C for 2 h under a reduced pressure of 10^{-6} Torr. A stoichiometric mixture of CO and O_2 ($\text{CO} + 1/2\text{O}_2$) at a pressure of 2 Torr was used. The kinetics of the catalytic reaction was monitored by measuring the pressure of the reaction mixture at different time intervals until no change in the pressure was attained. The produced CO_2 was removed from the reaction atmosphere by freezing at liquid nitrogen temperature. So, the percentage decrease of the pressure of the reacting gases at a given time interval

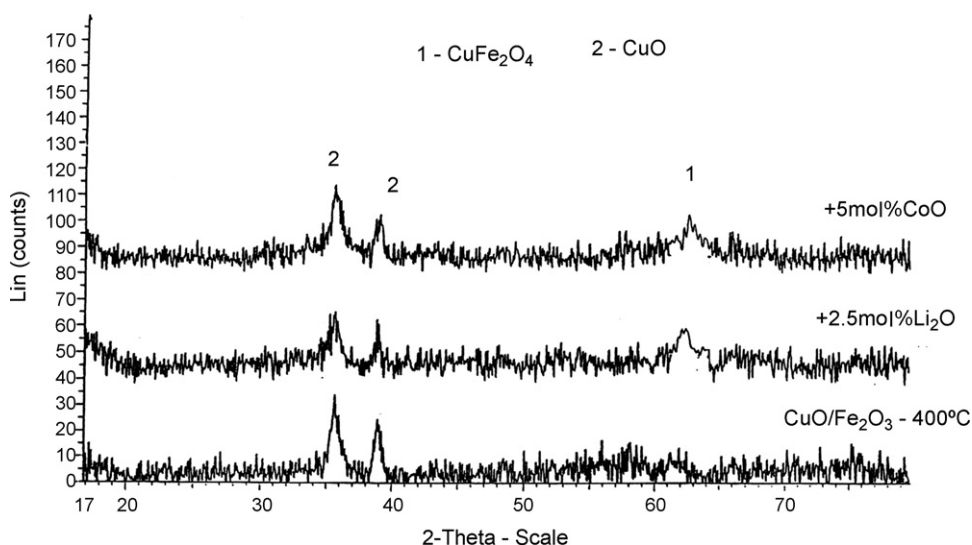


Fig. 1. XRD diffractograms of pure and Li_2O and CoO -doped $\text{CuO}/\text{Fe}_2\text{O}_3$ solids precalcined at 400°C .

determines the percentage conversion of the catalytic reaction at that time. The saturation vapour pressure of CO at $-196\text{ }^{\circ}\text{C}$ being 160 Torr makes its liquefaction at that temperature improbable under the employed conditions ($P = 2\text{ Torr}$) [25].

3. Results and discussion

3.1. XRD investigation of pure and variously doped solids

The X-ray diffractograms of pure and doped solids calcined at 400 and 600 $^{\circ}\text{C}$ were determined and depicted in Figs. 1 and 2, respectively. Examination of Fig. 1 shows the following: (i) the diffractogram of pure sample calcined in air at 400 $^{\circ}\text{C}$ consisted of diffraction lines of CuO phase having moderate degree of crystallinity which suffered a further slight decrease upon doping. (ii) The absence of all diffraction lines of Fe_2O_3 in pure and doped solids precalcined at 400 $^{\circ}\text{C}$ may indicate its presence in a very poorly crystalline state not detectable by X-ray diffractometer. (iii) Doping the system investigated with 2.5 mol% Li_2O or 5 mol% CoO led to the appearance of a new diffraction line at d-spacing of 1.61 \AA (which corresponds to copper ferrite phase, JCPDS files CuFe_2O_4 : 25–283). This finding indicates clearly that doping of $\text{CuO}/\text{Fe}_2\text{O}_3$ with Li_2O or CoO, followed by calcination at 400 $^{\circ}\text{C}$ stimulated the copper ferrite formation at relatively low temperature.

Examination of Fig. 2 shows that heating pure and doped solids at 600 $^{\circ}\text{C}$ did not lead to a complete conversion of reacting oxides into CuFe_2O_4 . The completion of such reaction may need a prolonged heating (few days) at 600 $^{\circ}\text{C}$ or heating at temperature above 600 $^{\circ}\text{C}$. In fact, diffractograms of pure and doped solids calcined at 600 $^{\circ}\text{C}$ consisted of all diffraction lines of CuFe_2O_4 , CuO and $\alpha\text{-Fe}_2\text{O}_3$ phases. However, doping the system investigated at 600 $^{\circ}\text{C}$ increased the degree of crystallinity of unreacted oxides and the produced copper ferrite.

Analysis of X-ray data permitted the determination of crystallite size of CuO, Fe_2O_3 and CuFe_2O_4 phases and the results are summarized in Table 1. Table 1 shows that: (i) the

Table 1

Crystallite size of different phases in $\text{CuO}-\text{Fe}_2\text{O}_3$ system as influenced by doping with Li_2O and CoO conducted at 400 and 600 $^{\circ}\text{C}$

Solid	Calcination temperature $^{\circ}\text{C}$	Crystallite size		
		CuO	Fe_2O_3	CuFe_2O_4
$\text{CuO}-\text{Fe}_2\text{O}_3$	400	31	–	–
+2.5 mol% Li_2O	–	43	–	–
+5.0 mol% CoO	–	40	–	–
$\text{CuO}-\text{Fe}_2\text{O}_3$	600	48	700	16
+2.5 mol% Li_2O	–	67	175	30
+5.0 mol% CoO	–	49	99	21

crystallite size of both CuO and CuFe_2O_4 phases is within the nanocrystalline range (16–67 nm). (ii) Li_2O -doping of the system investigated, followed by calcination at 600 $^{\circ}\text{C}$ led to an increase of about 87% and about 40% in the crystallite size of CuFe_2O_4 and CuO, respectively. (iii) CoO-doping carried out at 600 $^{\circ}\text{C}$ resulted in an increase of about 31% in the crystallite size of copper ferrite produced without much changing the crystallite size of CuO. (iv) On the other hand, Li_2O or CoO-doping carried out at 600 $^{\circ}\text{C}$ led to a considerable decrease in the crystallite size of unreacted $\alpha\text{-Fe}_2\text{O}_3$. The decrease was, however, more pronounced in the case of CoO-doping which brought about a considerable decrease of the crystallite size of $\alpha\text{-Fe}_2\text{O}_3$ from 700 to 99 nm and becoming a nanocrystalline solid. The resulting decrease in the crystallite size of $\alpha\text{-Fe}_2\text{O}_3$ due to doping the system investigated with small amounts of Li_2O or CoO might be considered as one of the factors that enhanced the solid–solid interaction between Fe_2O_3 with CuO producing CuFe_2O_4 phase. The other factors affecting the ferrite formation may be the dissolution of some of dopants added in the lattices of reacting oxides involved in copper ferrite formation.

Lithium and cobalt oxide dopants could be dissolved in the lattices of each reacting oxides involved in the forming copper ferrite. The dissolution process can be can be simplified by the

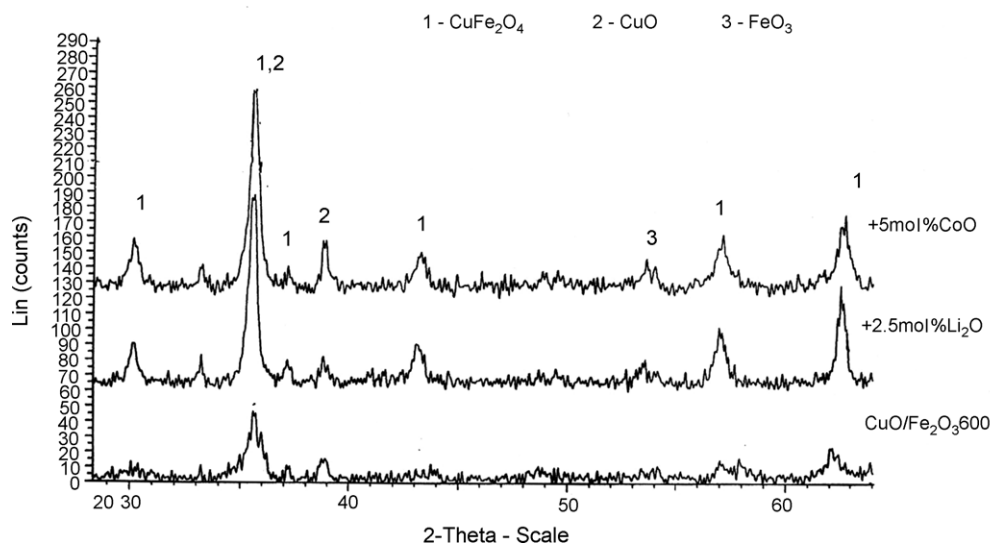
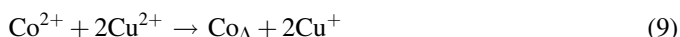
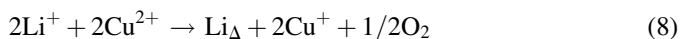
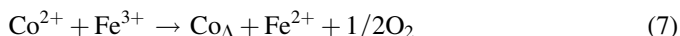
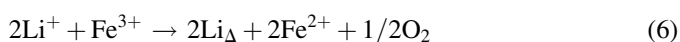
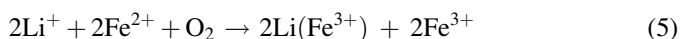
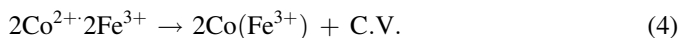
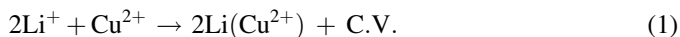


Fig. 2. XRD diffractograms of pure and Li_2O and CoO-doped $\text{CuO}/\text{Fe}_2\text{O}_3$ solids precalcined at 600 $^{\circ}\text{C}$.

use of Kröger's notations [26] in the following manner:



$\text{Li}(\text{Cu}^{2+})$ and $\text{Li}(\text{Fe}^{3+})$ are the monovalent lithium ions located in the positions of host copper and iron oxides in CuO and Fe_2O_3 , respectively; $\text{Co}(\text{Cu}^{2+})$, $\text{Co}(\text{Fe}^{3+})$ are divalent cobalt ions located in the positions of host copper and iron cations of CuO and Fe_2O_3 , respectively; Li_Δ and Co_Δ are lithium and cobalt ions located in the interstitial positions of copper and ferric oxide lattices; C.V. created cationic vacancies.

The dissolution of dopant ions in the lattices of reacting oxides according to reactions (1–4) which led to creation of cationic vacancies might increase the mobility of cations of reacting oxides thus enhancing the ferrite formation. Incorporation of lithium and cobalt dopant ions in Fe_2O_3 and CuO lattices according to reactions (6)–(9) decreased the number of reacting cations (Cu^{2+} and Fe^{3+}) involved in the ferrite formation. On the other hand, dissolution of lithium ions in ferric oxide lattice according to reaction (5) is expected to increase the number of Fe^{3+} via converting Fe^{2+} ion that may be present in Fe_2O_3 . So, reactions (1) and (3)–(5) might be expected to stimulate copper ferrite formation, while reactions (6)–(9) might exert an opposite effect. The fact that Li_2O or CoO-doping of CuO/ Fe_2O_3 system enhanced copper ferrite formation might suggest the domination of reactions (1) and (3)–(5).

3.2. EDX investigation of pure and doped solids

EDX investigation of pure and doped solids calcined at 400 and 600 °C was carried out. The atomic abundance of copper, iron, oxygen and cobalt (dopant) species present in the surface of the calcined solids is given in Table 2. It is well known that EDX technique supplies an accurate determination of the relative atomic concentration of different elements which are present on their surfaces. Inspection on the results given in Table 2 reveals the following: (i) the atomic ratio of Fe/Cu in surface of pure solids calcined at 400 and 600 °C determined by EDX is smaller than that found in bulk. The Fe/Cu ratio in the bulk of solids investigated has been readily determined on the basis of nominal composition of these solids. In fact, Fe/Cu ratio in bulk of pure solids calcined at 400 and 600 °C is 2:1, while it decreases to 1.53 and 1.44 in case of pure solids calcined at 400 and 600 °C,

Table 2

Surface molar concentration of pure CuO- Fe_2O_3 and that doped with Li_2O and CoO and heated at 400 and 600 °C determined by EDX

Solid catalyst	Calcination temperature °C	Element	Atomic abundance	
			Found	Calculated
CuO- Fe_2O_3	400	O	57	57
	–	Fe	26	29
	–	Cu	17	14
+2.5 mol% Li_2O	–	O	57	58
	–	Fe	30	28
	–	Cu	13	14
+5.0 mol% CoO	–	O	57	57
	–	Fe	29	26
	–	Cu	13	13
CuO- Fe_2O_3	600	O	56	57
	–	Fe	26	29
	–	Cu	18	14
+2.5 mol% Li_2O	–	O	57	58
	–	Fe	29	28
	–	Cu	14	14
+5.0 mol% CoO	–	O	57	57
	–	Fe	30	26
	–	Cu	12	13
CuO- Fe_2O_3	600	O	56	57
	–	Fe	26	29
	–	Cu	18	14
+2.5 mol% Li_2O	–	O	57	58
	–	Fe	29	28
	–	Cu	14	14
+5.0 mol% CoO	–	O	57	57
	–	Fe	30	26
	–	Cu	12	13
CuO- Fe_2O_3	600	O	56	57
	–	Fe	26	29
	–	Cu	18	14
+2.5 mol% Li_2O	–	O	57	58
	–	Fe	29	28
	–	Cu	14	14
+5.0 mol% CoO	–	O	57	57
	–	Fe	30	26
	–	Cu	12	13
CuO- Fe_2O_3	600	O	56	57
	–	Fe	26	29
	–	Cu	18	14
+2.5 mol% Li_2O	–	O	57	58
	–	Fe	29	28
	–	Cu	14	14
+5.0 mol% CoO	–	O	57	57
	–	Fe	30	26
	–	Cu	12	13
CuO- Fe_2O_3	600	O	56	57
	–	Fe	26	29
	–	Cu	18	14
+2.5 mol% Li_2O	–	O	57	58
	–	Fe	29	28
	–	Cu	14	14
+5.0 mol% CoO	–	O	57	57
	–	Fe	30	26
	–	Cu	12	13
CuO- Fe_2O_3	600	O	56	57
	–	Fe	26	29
	–	Cu	18	14
+2.5 mol% Li_2O	–	O	57	58
	–	Fe	29	28
	–	Cu	14	14
+5.0 mol% CoO	–	O	57	57
	–	Fe	30	26
	–	Cu	12	13
CuO- Fe_2O_3	600	O	56	57
	–	Fe	26	29
	–	Cu	18	14
+2.5 mol% Li_2O	–	O	57	58
	–	Fe	29	28
	–	Cu	14	14
+5.0 mol% CoO	–	O	57	57
	–	Fe	30	26
	–	Cu	12	13

respectively. This finding indicates a heterogeneous nature of coprecipitated mixed solids, i.e the chemical composition of their bulk is different from that of their surface. This difference might suggest the precipitation of ferric hydroxide (or hydrated ferric oxide) before the precipitation of copper hydroxide. (ii) Doping the system investigated with CoO or Li_2O , followed by calcination at 400 and 600 °C increased to a large extent Fe/Cu ratio; the increase was, however, more pronounced in case of cobalt oxide-doping. In fact, Fe/Cu ratio in pure mixed solids precalcined at 600 °C increases from 1.44 to 2.07 and 2.5 for the solids doped with 2.5 mol% Li_2O and 5.0 mol% CoO, respectively. This significant increase in Fe/Cu ratio due to doping might suggest an effective migration of Fe^{3+} from bulk of solids towards their surface and a possible migration of Cu^{2+} surface to bulk of these solids. The migration process might result from a concentration gradient of Fe^{3+} and Cu^{2+} ions in bulk and surface of doped solids. The creation of cationic vacancies in doped solids (c.f. reactions (1), (3) and (4)) enhanced the diffusion or migration of Fe^{3+} and Cu^{2+} from bulk to surface and from surface to bulk, respectively. (iii) The concentration of cobalt dopant species at surface and bulk of doped solids is 1 and 4 atom%, respectively for solids calcined at 400 or 600 °C. This finding was not expected simply because the doped solids were prepared by impregnation method [27] and dopant species might be preferentially retained on the surface of the doped samples. This discrepancy could be resolved by considering the contribution of most of cobalt species added in the formation of bulk mixed ferrite phase having the formula $\text{Co}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$. The close similarity between the diffraction data of copper ferrite and mixed ferrite phase makes their distinction a very difficult task.

3.3. Specific surface areas of pure and various doped solids calcined at 400 and 600 °C

The BET-surface areas of pure CuO/Fe₂O₃ and those doped with Li₂O or CoO calcined at 400 and 600 °C were determined. The computed S_{BET} values are given in Table 3. Examination of Table 3 shows the following: (i) the S_{BET} value of pure solids calcined at 400 °C indicates their porous nature and might suggest that they consisted of finely divided or nanocrystalline materials (c.f. Table 1). (ii) Li₂O or CoO-doping of the system investigated followed by calcination at 400 °C did not much affect its S_{BET} value. (iii) On the other hand, the doping process carried out at 600 °C brought about a measurable increase (about 47%) of the S_{BET} of doped solids. (iv) The increase in calcination temperature of pure and doped solids from 400 to 600 °C resulted in a considerable decrease in their S_{BET} values, this decrease attained 87 and 80% for pure and doped solids, respectively. The abrupt decrease in BET-surface areas of pure and doped solids upon increasing their calcination temperature from 400 to 600 °C might be attributed to an effective increase in degree of crystallinity of the treated solids and also to an increase in the crystallite size of different phases present.

3.4. Catalytic oxidation of CO by O₂ over pure and doped solids

The catalytic oxidation of CO by O₂ was conducted over pure CuO/Fe₂O₃ system and variously Li₂O and CoO-doped solids precalcined at 400 and 600 °C. First-order kinetics was observed in all cases, the slopes of the first-order plots determine the values of the reaction rate constant (k) at a given reaction temperature over a given catalyst sample. Fig. 3 shows representative first-order plots of CO oxidation by O₂ carried out at 100 and 200 °C over the catalyst samples calcined at 400 °C and 600 °C, respectively.

The role of Li₂O and CoO-treatment in the catalytic activity of CuO/Fe₂O₃ system is better investigated by comparing the values of reaction rate constant per unit surface area k^- as a function of dopant concentration in catalysts samples precalcined at 400 and 600 °C. The computed values of k^- were graphically illustrated in Fig. 4. This figure shows that: (i) the catalytic activity of the pure investigated system increased by 79% upon raising the calcination temperature from 400 to 600 °C. This pronounced increase in the catalytic activity can be attributed to the role of temperature in stimulation the

Table 3
Specific surface areas of various solid samples calcined at 400 and 600 °C

Solid adsorbent	Calcination temperature (°C)	S_{BET} (m ² /g)
CuO–Fe ₂ O ₃	400	142
+2.5 mol% Li ₂ O	–	139
+2.5 mol% CoO	–	139
+5.0 mol% CoO	–	132
CuO–Fe ₂ O ₃	600	19
+2.5 mol% Li ₂ O	–	28
+2.5 mol% CoO	–	27
+5.0 mol% CoO	–	36

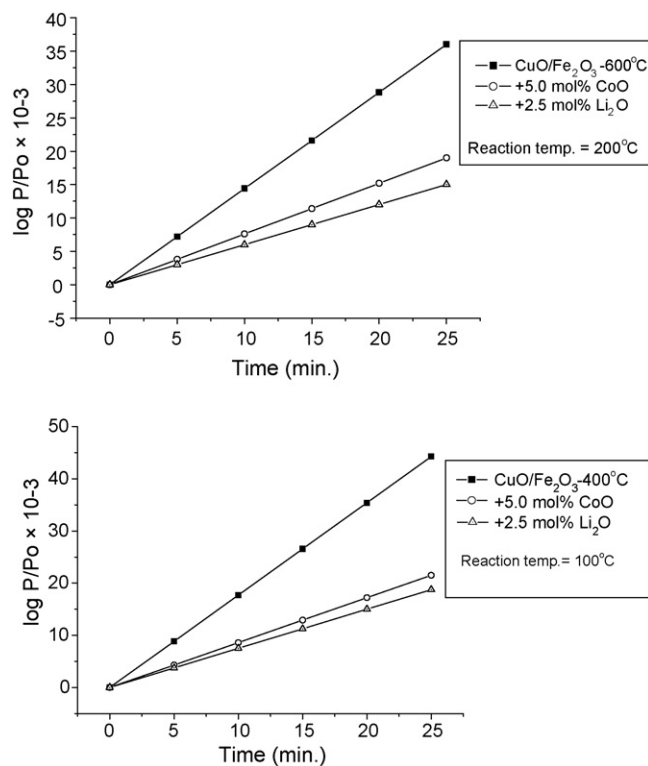


Fig. 3. First order plots of CO oxidation by O₂ over pure and variously doped solids precalcined at 400 and 600 °C, respectively.

formation of CuFe₂O₄ (as previously discussed in the XRD section). (ii) Doping of the investigated system with either 2.5 mol% Li₂O or 5.0 mol% CoO, followed by calcination at 400 °C led to a decrease in the catalytic activity of the mixed oxides system by about 35 and 32%, respectively. This decrease in the catalytic activity seems to run parallel to the role of both dopants in increasing the crystallite size of CuO as shown in Table 1. The crystallite size of CuO decreased by 39 and 29% upon doping the investigated system with 2.5 mol% Li₂O and 5.0 mol% CoO, respectively. (iii) Increasing the calcination temperature of Li₂O-doped system from 400 to 600 °C was accompanied by a limited decrease in its catalytic activity by

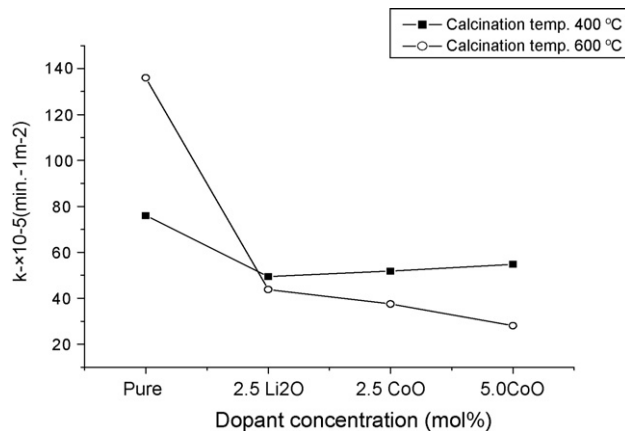


Fig. 4. Variation of the specific reaction rate constant k^- for the oxidation of CO by O₂ as a function of the dopant concentration. Catalytic reaction conducted at 140 °C.

Table 4

Activation energies ΔE of the catalytic oxidation of CO by O₂ conducted over pure CuO–Fe₂O₃ and Li₂O or CoO-doped catalysts calcined at 400 and 600 °C

Solid adsorbent	Calcination temperature (°C)	ΔE (kJ mol ⁻¹)
CuO–Fe ₂ O ₃	400	23
+2.5 mol% Li ₂ O	–	21
+2.5 mol% CoO	–	21
+5.0 mol% CoO	–	21
CuO–Fe ₂ O ₃	600	29
+2.5 mol% Li ₂ O	–	30
+2.5 mol% CoO	–	31
+5.0 mol% CoO	–	31

13%. In fact, it was expected that the catalytic activity of CuO/Fe₂O₃ system would be increased upon doping with Li₂O due to its stimulation of copper ferrite formation, but the results were opposite to this expectation. One of the authors [21] has reported that XRD investigation showed the formation of lithium ferrite at 700 °C. So, this decrease in the catalytic activity may be attributed to a possible formation of a surface layer of LiFe₅O₈ in doped solids calcined at calcination 600 °C whose amount is below the detection limit of the X-ray diffractometer. The formed LiFe₅O₈ seems to be catalytically inactive towards CO oxidation by O₂. (iv) Raising the calcination temperature of CoO-doped solids from 400 to 600 °C decreased the catalytic activity to an extent proportional to the amount of CoO added. The decrease attained 28 and 49% in presence of 2.5 and 5.0 mol% CoO, respectively. This decrease may be attributed to the formation of surface Co_xCu_{1-x}Fe₂O₄, as discussed in the EDX section. In order to obtain experimental evidence showing that the catalytic activity of cobalt copper mixed ferrite phase is smaller than that of CuFe₂O₄, an additional sample of CoFe₂O₄ was prepared using the same conditions, followed in the preparation of CuFe₂O₄. This particular sample being calcined at 600 °C measured S_{BET} value of 52 m²/g instead of 19 m²/g for CuFe₂O₄ calcined at 600 °C. CO oxidation by O₂ was carried out at 200 °C over pure CoFe₂O₄ –600°C. The computed k^- value was found to be $77 \times 10^{-5} \text{ min}^{-1} \text{ m}^{-2}$ instead of $379 \times 10^{-5} \text{ min}^{-1} \text{ m}^{-2}$ for CuFe₂O₄. These findings indicate clearly that the contribution of cobalt dopant species in the formation of cobalt–copper mixed ferrite phase should be normally accompanied by a significant drop in the catalytic activity of the cobalt-doped ferrite sample. So, the observed measurable decrease in the catalytic activity of CuFe₂O₄ due to doping with CoO might be attributed to a conversion of a portion of catalytically active copper ferrite phase into cobalt–copper mixed ferrite phase.

Determination of the apparent activation energy (ΔE) for the catalysis of CO- oxidation by O₂ over pure and variously doped solids investigated could shed some light on the possible change in the mechanism of the catalyzed reaction and hence give useful information about the possible change in the concentration of catalytically active constituents. The values of reaction rate constant (k) of the catalytic reaction measured at different temperatures over various solids allow ΔE to be calculated by direct application of the Arrhenius equation. The

computed ΔE values are listed in Table 4. Inspection of Table 4 reveals that the values of ΔE fluctuated between 23–21 and from 29–31 kJ/mol for catalysts precalcined at 400 and 600 °C, respectively. The fluctuation of ΔE values was within the range of experimental error ($\pm 2 \text{ kJ mol}^{-1}$), i.e., ΔE was nearly constant for the catalytic reaction in question. These findings enabled us to suggest that doping the investigated system with either Li₂O or CoO, followed by heating at 400 and 600 °C did not change the mechanism of the catalyzed reaction but rather changed the concentration of catalytically active sites involved in chemisorption and catalysis of CO oxidation by O₂.

4. Conclusions

The results obtained permitted to draw the following main conclusions:

- Doping CuO/Fe₂O₃ system with Li₂O or CoO, followed by calcination at 400 and 600 °C led to dissolution of some of dopants in the CuO and Fe₂O₃ lattices via different mechanisms. Some of these processes created cationic vacancies leading to an increase in the mobility of reacting oxides. This effect enhanced the ferrite formation.
- Pure and variously doped solids calcined at 600 °C led to the formation of nanocrystalline CuFe₂O₄.
- A limited portion of CoO was dissolved in the individual oxide lattices, while the other portion contributes in the formation of a mixed ferrite Co_xCu_{1-x}Fe₂O₄.
- Raising the calcination temperature from 400 to 600 °C led to a drastic decrease in the S_{BET} of pure and doped solids.
- The doping process carried out at 600 °C brought about a measurable increase in the S_{BET} of doped solids.
- The raise in precalcination temperature from 400 to 600 °C and doping with either Li₂O or CoO brought about a measurable decrease in the catalytic activity of the system investigated.
- CuFe₂O₄ showed a catalytic activity, in CO oxidation by O₂, smaller than those of individual oxides (CuO and Fe₂O₃).
- The doping process of the system investigated, followed by calcination at 400 and 600 °C did not change the mechanism of the catalytic reaction but rather alter the concentration of active sites involved in the catalytic reaction.

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