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Surface and catalytic properties of CuO and Co_3O_4 solids as influenced by treatment with Co^{2+} and Cu^{2+} species

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Abstract

The effects of treatment CuO and Co_3O_4 solids with Co^{2+} and Cu^{2+} ions on their surface and catalytic properties were investigated using nitrogen adsorption at $-196\,^\circ$C, the oxidation of CO by O_2 at 100–250 $^\circ$C and the decomposition of H_2O_2 at 30–50 $^\circ$C. Pure and doped CuO and Co_3O_4 solids were subjected to heat treatment at 300–700 $^\circ$C and the dopant concentration was varied between 1.0 and 7.5 mol%.

The results obtained revealed that the doping process of the investigated solids increased the degree of crystallinity and particle size of CuO and Co_3O_4 phases. This treatment led also to a progressive decrease in the specific surface areas (S_{BET}) of the treated adsorbents to an extent proportional to the amount of dopants added. However, doping of Co_3O_4 and CuO solids with small amounts of Cu^{2+} and Co^{2+} ions, respectively, much increased their catalytic activities in H_2O_2 decomposition. On the other hand, the doping process brought about both increase and decrease in their catalytic activities towards CO oxidation by O_2 depending on both the nature of the treated solids and that of dopant ions and the calcination temperature. Also, the doping process did not modify the mechanism of the catalytic reactions but changed the concentration of catalytically active sites involved in the catalyzed reactions.
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1. Introduction

Catalytic oxidation reactions are extensively used for industrial synthesis of chemicals and environmental pollution control. Typical oxidation catalysts are metal oxides and pure metals on which chemisorbed oxygen is the oxidizing species [1–7]. With metal oxides the nature of the reacting oxygen species is less obvious. In addition to adsorbed surface species, lattice oxygen can participate in the reaction depending on the oxide used and the temperature of the catalyzed reaction [8–11]. Catalytic oxidation is the process thought by many research studies to curb CO emissions of combustion engines into the atmosphere [12]. Oxidation of carbon monoxide has been carried out on various catalysts. These catalysts are precious metals [13,14] and transition metal oxide catalysts [15–20].

The activity of a catalyst is sometimes remarkably improved by combining more than two elements (synergism) [21–24]. Copper oxide has been demonstrated to be a very active species among the base-metal oxides as oxidation catalysts [25–28]. Copper and cobalt oxides are the most widely used catalysts because of their high activities and selectivities as

oxidation–reduction catalysts. The oxidation state of copper changes thermodynamically between CuO, Cu_2O and Cu as a functions of temperature and oxygen partial pressure [29–32], while the oxidation state of cobalt changes between CoO, Co_3O_4 and Co [33–36]. The differences in oxygen defects, oxygen holes and oxygen adsorbed species in these oxidation states are thought to be the main reason for the high activity or selectivity of such catalysts.

Copper catalysts supported on alumina-based mixed oxides (Cu/Al_2O_3-MO; M = Al, Ce, Co, Cr, Fe, Mg, Mn, Sm, Zn and Zr) were investigated for CO removal in the methanol steam reformed gas. Cu-ZnO/Al_2O_3 exhibited an excellent activity. The order of the activity for Cu/Al_2O_3-MO with different M follows the sequence: Zn > Al > Cr > Mn > Mg. The highest catalytic activity is strongly related to the particle size of Cu [37]. The catalytic oxidation of carbon monoxide by a composite oxide catalyst containing equimolar ratio of silver and cobalt was studied [38]. XRD, XPS and TGA investigations indicated that the composite oxide is not a physical mixture of silver and cobalt oxides and that silver is stabilized in an oxide in the presence of cobalt at temperatures as a high as 800 °C.

The present work aimed to investigate the role of small amounts of Co^{2+} or Cu^{2+} additives in modifying the surface and catalytic properties of CuO or Co_3O_4 solids, respectively. The techniques employed were XRD, nitrogen adsorption at −196 °C, oxidation of CO by O_2 at 100–250 °C and H_2O_2 decomposition at 30–50 °C.

2. Experimental

2.1. Materials

Pure CuO samples were prepared by the thermal decomposition of basic copper carbonate at 300, 500 and 700 °C. Samples doped with cobalt were obtained by treating a known mass of finely powdered basic copper carbonate with a calculated amount of cobalt nitrate, $Co(NO_3)_2 \cdot 6H_2O$, dissolved in the least amounts of distilled water necessary to make a paste. The paste was dried at 100 °C to constant weight, then heated in air for 5 h at 300, 500 and 700 °C, respectively. The nominal concentration of cobalt in the doped samples

expressed as mol% CoO was 1.0, 2.5, 5.0 and 7.5, respectively.

Pure cobalt oxide samples were prepared by thermal decomposition of basic cobalt carbonate at 300 and 700 °C. The variously doped solid samples were obtained by treating a known weight of finely powdered basic cobalt carbonate with calculated amounts of copper nitrate dissolved in the least amount of distilled water making a paste. The paste was dried at 100 °C to a constant weight then heated in air at 300 and 700 °C for 5 h. The concentrations of CuO dopant expressed as mol% were 2.5, 5.0 and 7.5. All chemicals employed were of analytical grade as supplied by Merck and Prolabo Ltd.

2.2. Techniques

An X-ray investigation of pure and variously doped solid samples preheated in air at 300–700 °C was carried out using a Philips diffractometer (type PW 1390). The patterns were run with Fe-filtered cobalt ($\lambda = 1.7889$ Å) for pure and variously treated Co_3O_4 solids at 30 kV and 10 mA with a scanning speed of $2°$ in 2θ min^{-1}, while Ni-filtered copper radiation ($\lambda = 1.5405$ Å) was employed for pure and variously treated CuO solids. The particle size of the investigated solids was calculated from the X-ray line broadening analysis of some diffraction lines of CuO and Co_3O_4 phases using the Scherrer equation [39]:

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

where d is the mean crystallite diameter, λ the X-ray wavelength, K the Scherrer constant (0.89) and $B_{1/2}$ the full width half maximum (FWHM) of the copper and cobalt diffraction lines and θ the different angle. In line broadening analysis the scanning rate was fixed at $0.2°$ in 2θ min^{-1}.

The surface properties of the pure and variously doped solid samples were determined from nitrogen adsorption isotherms measured at −196 °C using a 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 was carried out on various catalysts at temperatures between 100 and 250 °C using a static method. A fresh 200 mg catalyst sample was employed in each kinetic experiment

and was activated by heating at 250 or 300 °C for 2 h under a reduced pressure of 10^{-6} Torr. The kinetics of the catalytic reaction were monitored by measuring the pressure of the reaction mixture (2 Torr of $CO + 1/2O_2$) 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 determines the percentage conversion of the catalytic reaction at that time.

The catalytic activities of different catalyst samples were also determined by studying the decomposition of H_2O_2 in their presence at temperatures within 30–50 °C using 50 mg of a given catalyst sample with 0.5 ml volume of H_2O_2 of known concentration diluted to 20 ml with distilled water. The reaction kinetics were monitored by measuring the volume of oxygen gas liberated at different time intervals until equilibrium was attained.

3. Results and discussion

3.1. XRD investigation of pure and variously doped solids precalcined at 300–700 °C

The X-ray diffractograms of pure and variously doped solids precalcined at 300–700 °C were measured. Fig. 1 shows X-ray diffractograms of pure and heavily doped CuO solid samples precalcined at 300 and 700 °C. Inspection of this figure revealed that the pure solid samples preheated at 300 and 700 °C consisted of CuO phase of higher degree of crystallinity, while the heavily doped solids (treated with 7.5 mol% CoO) consisted of CuO phase besides Co_3O_4 as separate phase. The absence of any diffraction line of Co_3O_4 phase in the sample doped with 5.0 mol% CoO might suggest a complete dissolution of the doped oxide in CuO lattice forming CoO–CuO solid solution and/or the presence of dopant oxide as a separate phase with a small concentration below the detection limit of X-ray diffractometer. The formula of the produced solid solution may be written as $Co_xCu_{1-x}O$, where $x \leq 0.05$. The detection of cobaltic oxide as a separate phase in the sample doped with 7.5 mol% CoO might indicate that the maximum amount of cobalt oxide that dissolved in CuO lattice by heat
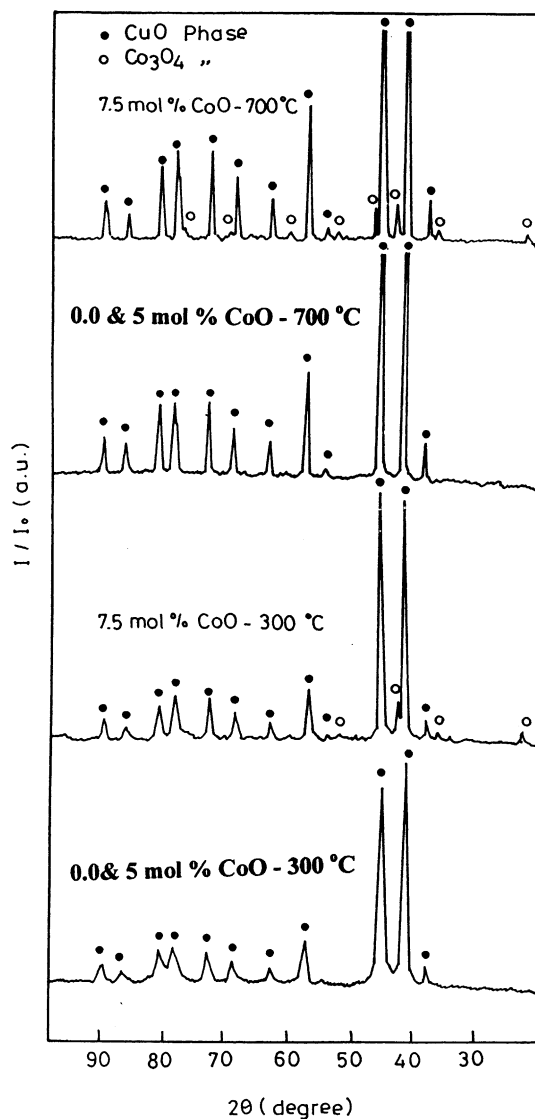

Fig. 1. X-ray diffractograms of pure and heavily doped CuO solid samples precalcined at 300 and 700 °C.

treatment at 300–700 °C is limited and did not exceed 5.0 mol%. The increase in the amount of CoO added and calcination temperature of the solids investigated up to 700 °C resulted in a significant increase in the degree of crystallinity of the produced CuO phase. In fact, the addition of increasing amounts of CoO followed by calcination at 300–700 °C resulted in a progressive increase in the relative intensity of all

diffraction lines (a measure for the degree of crystallinity) of CuO phase. The peak height of the main diffraction lines of CuO phase located at 2.50, 2.32 and 1.50 Å increased from 186 to 210, 166 to 212 and 37 to 43 (a.u.), respectively, upon the addition of 7.5 mol% CoO for CuO solids precalcined at 300 °C. Similar trend was observed in the case of the heavily doped sample precalcined at 700 °C. These findings indicate clearly that CoO doping of CuO conducted at 300 and 700 °C much increased the degree of ordering or degree of crystallinity of CuO phase. The effect of this treatment on the particle size of CuO crystallites has been also investigated by measuring the average particle size of CuO phase in pure and heavily doped samples calcined at 300 °C. This has been done by using X-ray line broadening analysis. The computed values of the particle size of CuO phase were 80, 130, 140 and 160 Å in the pure sample and those treated with 2.5, 5.0 and 7.5 mol% CoO precalcined at 300 C°, respectively. So, it can be concluded that CoO doping of CuO solids followed by calcination at 300 and 700 °C brought about a significant increase in the degree of crystallinity and particle size of CuO phase. Fig. 2 depicts the X-ray diffractograms of pure Co_3O_4 and heavily doped solids with CuO (7.5 mol%) preheated at 300 and 700 °C. It is seen from Fig. 2 that the XRD patterns of investigated solids precalcined at 300 and 700 °C are similar to each other and consisted mainly of all diffraction lines of Co_3O_4 phase. The disappearance of all diffraction lines characteristics for CuO phase in all solids investigated even those treated with 7.5 mol% CuO might suggest a complete dissolution of the dopant oxide in Co_3O_4 lattice forming $CuO–Co_3O_4$ solid solution having the formula $Cu_xCo_{3-x}O_4$, where x varies between 0.025 and 0.075. The rise in precalcination temperature of the solids investigated from 300 to 700 °C and the addition of increasing amounts of CuO followed by precalcination at 300–700 °C resulted in a progressive increase in the relative intensity of the diffraction lines of Co_3O_4 phase. This conclusion was evidenced by following up the increase in the peak height of the main diffraction lines Co_3O_4 due to these treatments. The peak height of the main lines of Co_3O_4 phase located at 4.66, 2.84 and 2.01 Å increased from 36 to 53, 48 to 78 and 37 to 59 (a.u.), respectively, upon the addition of 7.5 mol% CuO for Co_3O_4 solids precalcined at 300 °C. While the peak height of the lines
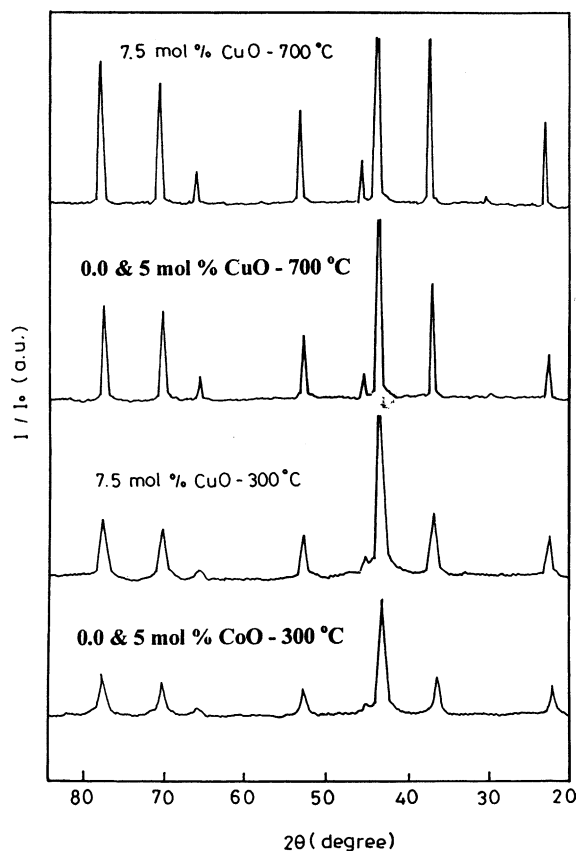

Fig. 2. X-ray diffractograms of pure and heavily doped Co_3O_4 solid samples precalcined at 300 and 700 °C. All lines refer to Co_3O_4 phase.

located at the same d-spacings increased from 56 to 107, 145 to 222 and 80 to 119 (a.u.), respectively, upon the addition of 7.5 mol% CuO for the solid samples precalcined at 700 °C. These results may indicate that CuO doping of Co_3O_4 followed by calcination at 300 and 700 °C effected a significant increase in the degree of crystallinity of Co_3O_4 phase. This behavior which is similar to that observed in the case of CoO doping of CuO conducted at 300 and 700 °C could be attributed to the formation of $Cu_xCo_{3-x}O_4$ solid solutions. The effect of this treatment on the particle size of Co_3O_4 phase has been investigated in the case of pure and doped solids precalcined at 300 °C. The results obtained revealed that the particle size of Co_3O_4 phase increased from 115 to 135 Å upon doping with 7.5 mol% CuO. It can thus be concluded

that treatment of Co_3O_4 with small amount of CuO (2.5–7.5 mol%) followed by calcination at 300 or 700 °C resulted in an increase the particle size and degree of crystallinity of Co_3O_4 phase. The observed changes in the degree of crystallinity and particle size of CuO and Co_3O_4 phases due to doping and calcination at 300 and 700 °C which led to the formation of solid solutions ($Co_xCu_{1-x}O$ or $Cu_xCo_{3-x}O_4$) are expected to modify the surface and catalytic properties of the treated solids.

3.2. Specific surface areas of the investigated solid samples

The BET surface areas of the investigated adsorbents were calculated from the linear BET plots and the data obtained is given in Table 1. The accuracy of this method is within about 3% and permits the determination of the total (external and internal) specific surface areas of the investigated adsorbents. The specific surface areas of CuO and Co_3O_4 due to doping with cobalt and copper ions followed by calcination at 300–700 °C were found to suffer a progressive decrease to an extent proportional to the amount of dopants added. However, no measurable change in the BET surface area of CuO due to treatment with cobalt ions conducted at 300 °C. The maximum decrease in the S_{BET} of Co_3O_4 and CuO due to doping with copper or cobalt ions followed by calcination at 300 and 700 °C attained 20 and 37% for the first adsorbent, and 35 and 33% for the second adsorbent, respectively. The observed decrease in the S_{BET} of both CuO

and Co_3O_4 due to doping might be discussed in terms of an effective increase in the particle size of both phases and possible formation of solid solutions. In fact, X-ray line broadening analysis of treated solids (CuO and Co_3O_4) followed by calcination at different temperatures indicated a significant increase in the particle size of CuO and Co_3O_4 phases. The observed increase in the particle size of these two phases should be accompanied by a significant decrease in the external specific surface areas of the treated solids.

3.3. Catalytic activity of pure and treated solid catalysts

The catalytic oxidation of CO by O_2 and H_2O_2 decomposition were carried out over pure and variously doped solids precalcined at different temperatures.

3.3.1. Catalytic oxidation of CO by O_2 over the pure and treated solids

The catalytic oxidation of CO by O_2 over pure and doped solids precalcined at 300, 500 and 700 °C was conducted at 100–250 °C. The results showed that the catalysis of CO oxidation by O_2 follows first-order kinetics over various investigated catalysts. Fig. 3 depicts representative first-order plots of CO oxidation by O_2 conducted at 150 and 225 °C over pure and doped CuO solids precalcined at 300 and 700 °C, respectively, and at 200 °C over pure and doped Co_3O_4 solids precalcined at 700 °C. The slope of the first-order plots determines the magnitude of the reaction rate constant (k) of the catalyzed reaction carried out at a given temperature. The values of k of the catalyzed reaction conducted over pure and treated solid catalysts precalcined at 300, 500 and 700 °C were determined. The variation of k for the reaction conducted at 100–250 °C as a function of dopant concentration is graphically illustrated in Fig. 4 for pure and different doped solids precalcined at 300–700 °C. It is seen from Fig. 4 that cobalt oxide doping of CuO solids followed by calcination at 300 °C resulted in a progressive decrease in the catalytic activity of the treated solids while heating the doped solids at 500 and 700 °C effected a remarkable progressive increase in the catalytic activity of the treated solids. The maximum decrease in the value of $k_{130\,°C}$, $k_{150\,°C}$ and $k_{170\,°C}$ due to doping with 7.5 mol% CoO attained 74, 68 and 61% for the solids

Table 1
Specific surface areas of pure and doped solids calcined at different temperatures

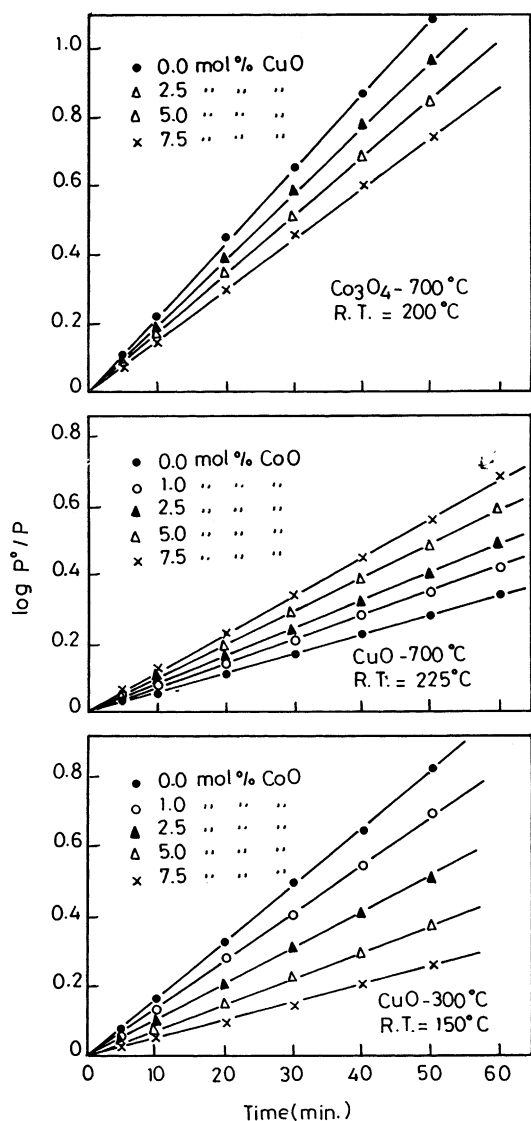| Catalyst	S_{BET} (m² g⁻¹)		
	300 °C	500 °C	700 °C
Pure CuO	33	31	24
+1.0 mol% CoO	32	28	22
+2.5 mol% CoO	31	25	20
+5.0 mol% CoO	31	23	18
+7.5 mol% CoO	30	20	16
Pure Co₃O₄	90		54
+2.5 mol% CuO	83		49
+5.0 mol% CuO	79		40
+7.5 mol% CuO	72		34

Fig. 3. First-order plots of CO oxidation by O_2 conducted at different temperatures over pure and variously doped cobalt and copper oxide catalysts.

precalcined at 300 °C, respectively. The maximum increase in the value of $k_{175 °C}$, $k_{200 °C}$ and $k_{225 °C}$ due to doping with 7.5 mol% CoO attained 143, 90 and 63% for the solids precalcined at 500 °C, respectively. While for the solids precalcined at 700 °C the maximum increase in the value of $k_{200 °C}$, $k_{225 °C}$ and $k_{250 °C}$ attained 185, 98 and 69%, respectively, due to doping with 7.5 mol% CoO. The observed significant

decrease in the catalytic activity of CoO-doped CuO solids calcined at 300 °C in CO oxidation by O_2 might be attributed to the following: (i) the observed effective increase in the degree of crystallinity of the CuO phase (cf. Fig. 1) and increase in its particle size (from 80 to 160 Å); and (ii) the possible formation of an amorphous copper cobaltite phase which has smaller catalytic activity than those of free oxides towards CO oxidation by O_2. So, the conversion of some of surface CuO into an amorphous copper cobaltite might be accompanied a decrease in its catalytic activity. The significant effective increase in the catalytic activity of CuO solids doped with Co^{2+} ions followed by calcination at 500 and 700 °C can be attributed to: (i) the thermal decomposition of copper cobaltite into finely divided Co_3O_4 and CuO separate oxides that having higher catalytic activity towards CO oxidation than that of the cobaltite phase; and (ii) the presence of most active sites Co_3O_4 on the top surface layers of the treated solids which enhanced the chemisorption of carbon monoxide and desorption of the produced CO_2. Fig. 4 shows also that CuO doping of Co_3O_4 solids followed by heat treatment at 300 and 700 °C resulted in a measurable decrease in the catalytic activity of the treated solids. The decrease was, however, more pronounced for the solids precalcined at 700 °C. The observed decrease in the catalytic activity of Co_3O_4 due to doping with CuO conducted at 300 and 700 °C might be attributed to the presence of CuO crystallites that cover an important portion of the surfaces of Co_3O_4 solid. This speculation may come from the treatment of Co_3O_4 solid with copper nitrate solution via wet impregnation method followed by heat treatment at 300 and 700 °C. The impregnation method of catalyst preparation is normally accompanied by a preferential retention of the dopant species of the top surface layers of the treated solids [40]. The fact that CuO catalyst exhibits a catalytic activity in CO oxidation by O_2 much smaller than that measured for Co_3O_4 may account for the observed decrease in the catalytic activity of Co_3O_4 due to doping with CuO. Furthermore, the observed decrease in the catalytic activity of Co_3O_4 by treatment with small mounts of CuO can be also attributed to the role of CuO dopant in increasing the particle size and degree of crystallinity of Co_3O_4 phase as mentioned before in the present work. In order to account for the observed decrease
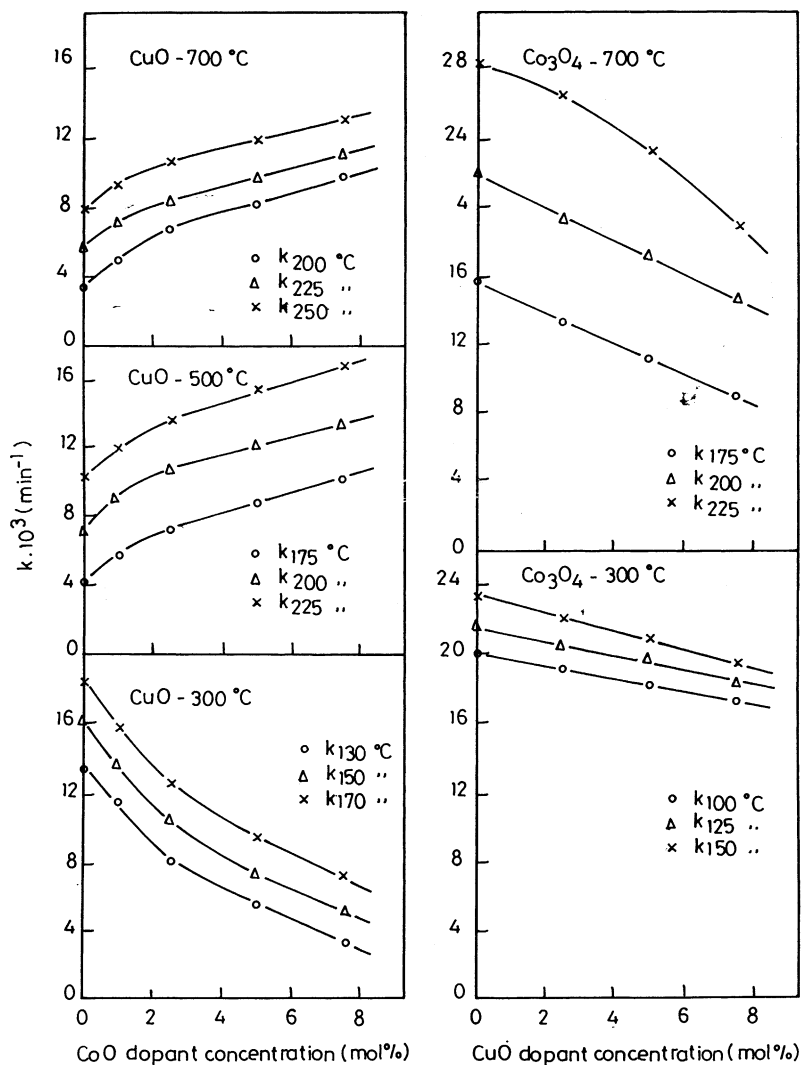
Fig. 4. Variation of reaction rate constant (k) as a function of dopant concentration for CO oxidation by O_2 conducted at different temperatures over pure and variously doped cobalt and copper oxide catalysts.

in the S_{BET} of various solids due to the treatment followed by calcination at different temperatures, the reaction rate constant per unit surface area ($\bar{k}$) was calculated for each catalyst sample and data obtained is given in Table 2. The computed values of $\bar{k}$ for CO oxidation by O_2 clearly indicate that the observed changes in the catalytic activities of the investigated solids due to the doping process were not attributed to the observed changes in the S_{BET} of the treated solids.

Determination of apparent activation energy ΔE for the catalysis of CO oxidation by O_2 over the variously doped solids has shed some light on the possible change in the mechanism of the catalyzed reaction and given useful information about the possible change in the concentration and nature of the catalytically active constituent. The values of k measured at 100–250 °C over the variously doped solid samples calcined at 300–700 °C have enabled ΔE to be calculated by direct application of the Arrhenius

Table 2

Reaction rate constant per unit area ($\bar{k}$, $\times 10^3$ min^{-1} m^{-2}) for the catalytic oxidation of CO by O$_2$ over pure and treated solids precalcined at 300–700 °C

Catalyst	300 °C			500 °C			700 °C		
	$\bar{k}_{130\,°C}$	$\bar{k}_{150\,°C}$	$\bar{k}_{170\,°C}$	$\bar{k}_{175\,°C}$	$\bar{k}_{200\,°C}$	$\bar{k}_{225\,°C}$	$\bar{k}_{200\,°C}$	$\bar{k}_{225\,°C}$	$\bar{k}_{250\,°C}$
Pure CuO	2.06	2.48	2.80	0.68	1.15	1.66	0.71	1.19	1.63
+1.0 mol% CoO	1.84	2.16	2.48	1.04	1.64	2.14	1.14	1.64	2.16
+2.5 mol% CoO	1.32	1.71	2.05	1.46	2.18	2.72	1.73	2.10	2.70
+5.0 mol% CoO	0.90	1.19	1.53	1.93	2.65	3.30	2.28	2.72	3.33
+7.5 mol% CoO	0.58	0.88	1.20	2.55	3.38	4.20	3.03	3.53	4.13
	$\bar{k}_{100\,°C}$	$\bar{k}_{125\,°C}$	$\bar{k}_{150\,°C}$				$\bar{k}_{175\,°C}$	$\bar{k}_{200\,°C}$	$\bar{k}_{225\,°C}$
Pure Co$_3$O$_4$	1.11	1.19	1.30				1.45	2.04	2.62
+2.5 mol% CuO	1.16	1.23	1.33				1.36	1.99	2.70
+5.0 mol% CuO	1.16	1.25	1.32				1.40	2.15	2.91
+7.5 mol% CuO	1.22	1.28	1.36				1.34	2.18	2.78

equation. The computed values of ΔE are listed in Table 3. Inspection of the data listed in Table 3 shows that: (i) Cobalt oxide doping (1.0–7.5 mol%) of CuO system followed by calcination at 300 °C brought about a progressive increase in the ΔE values (from 11.3 to 27 kJ mol^{-1}). These results express the observed progressive decrease in catalytic activity of the investigated solids due to doping with CoO. (ii)

Table 3

Activation energies (ΔE and ΔE^*) and frequency factor for the catalytic oxidation of CO by O$_2$ over pure and treated solid catalysts calcined at different temperatures

Catalyst	Calcination temperature (°C)	ΔE (kJ mol^{-1})	ln A	ΔE^* (kJ mol^{-1})	Constants h and a
Pure CuO	300	11.9	−0.73	11.9	$h = 0.24$, $a = 2.35 \times 10^{-2}$
+1.0 mol% CoO	300	11.3	−1.05	12.4	
+2.5 mol% CoO	300	15.7	−0.06	13.4	
+5.0 mol% CoO	300	19.3	0.61	14.7	
+7.5 mol% CoO	300	27.1	2.47	15.8	
Pure CuO	500	33.5	3.59	33.5	$h = 0.21$, $a = 1.2 \times 10^{-2}$
+1.0 mol% CoO	500	26.8	2.16	32.5	
+2.5 mol% CoO	500	23.2	1.40	31.8	
+5.0 mol% CoO	500	20.2	0.75	31.6	
+7.5 mol% CoO	500	18.9	0.51	31.0	
Pure CuO	700	46.9	6.21	46.9	$h = 0.45$, $a = 1.2 \times 10^{-2}$
+1.0 mol% CoO	700	26.8	1.56	46.0	
+2.5 mol% CoO	700	19.3	−0.09	45.3	
+5.0 mol% CoO	700	15.7	−0.81	44.7	
+7.5 mol% CoO	700	12.7	−1.40	44.1	
Pure Co$_3$O$_4$	300	3.9	−2.67	3.9	
+2.5 mol% CuO	300	3.6	−2.80	4.0	
+5.0 mol% CuO	300	3.3	−2.92	4.1	
+7.5 mol% CuO	300	3.3	−2.99	4.4	
Pure Co$_3$O$_4$	700	21.9	1.76	21.9	$h = 0.20$, $a = 7 \times 10^{-2}$
+2.5 mol% CuO	700	25.9	2.66	22.3	
+5.0 mol% CuO	700	27.8	3.04	22.8	
+7.5 mol% CuO	700	27.2	2.72	23.4	

The doping of CuO with cobalt oxide followed by calcination at 500 and 700 °C resulted a progressive decrease in the ΔE values. These results ran parallel to the observed progressive increase in the catalytic activity of the investigated solids. (iii) The doping of Co_3O_4 with CuO (2.5–7.5 mol% CuO) followed by precalcination at 700 °C led to a progressive increase in the ΔE values (from 21.9 to 27.2 kJ mol^{-1}), while ΔE values for the solids calcined at 300 °C remained virtually unchanged (within the experimental error

3.6 ± 0.3 kJ mol^{-1}). These findings indicate that a progressive decrease in the catalytic activity of the investigated solids precalcined at 700 °C while for solids calcined at 300 °C, the effect of doping in the catalytic activity was limited. This apparent discrepancy is resolved when the value of the logarithm of pre-exponential constant (A) in the Arrhenius equation is taken into account. Such data which is listed in Table 3 shows that, for all the systems investigated, the values of ln A varied considerably for each system
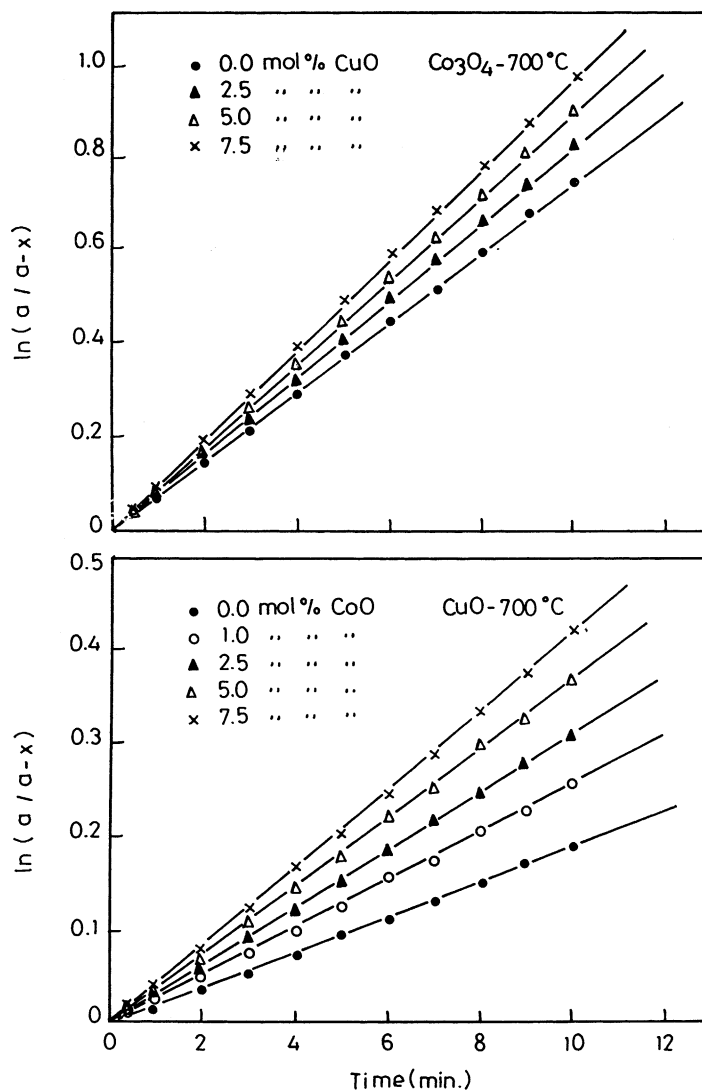

Fig. 5. First-order plots of H_2O_2 decomposition at 30 °C over pure and variously doped Co_3O_4 and CuO catalysts precalcined at 700 °C.

calcined at a given temperature but with different concentrations of the catalytically active constituent, thereby demonstrating the heterogeneity of the catalyst surface.

To account for this heterogeneity, the activation energies for the catalytic reaction were calculated adopting the values of $\ln A$ for the untreated catalyst solids

calcined at 300, 500 and 700 °C, respectively, for the other doped catalysts samples precalcined at the same temperatures. The resulting ΔE^* values obtained were virtually the same for the pure and variously doped solids precalcined at the same temperatures. This indicates that the treatment of CuO and Co_3O_4 solids with Co^{2+} or Cu^{2+} species did not change the mechanism
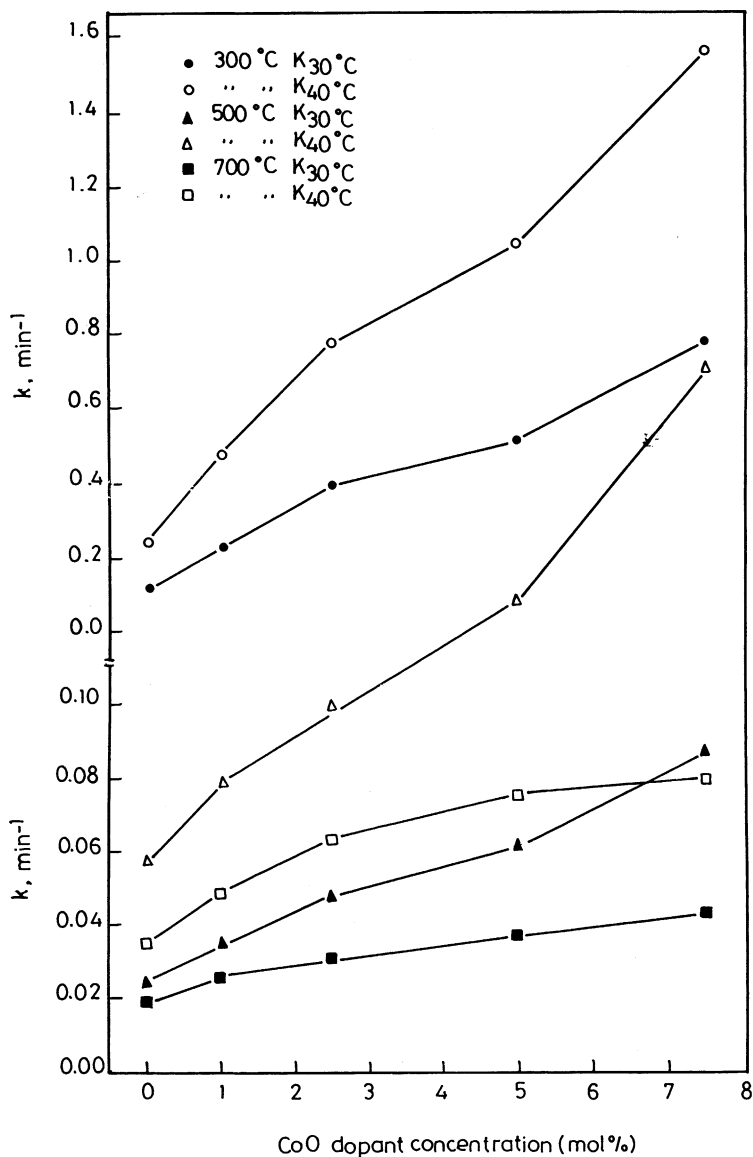

Fig. 6. Variation of reaction rate constant (k) as a function of dopant concentration for H_2O_2 decomposition at 30 and 40 °C over pure and variously doped CuO catalysts precalcined at 300–700 °C.

of the catalytic reaction but rather increased the concentration of catalytically active sites on the catalyst surface. This conclusion is also further supported by analysis based on the dissipation function for the energy of the active sites arising from the surface heterogeneity suggested by Balandin [41] and Ahuja et al. [42]:

$$f(E_i) = a \exp(hE_i)$$

where E_i is the interaction energy of the site i with the substrate. This equation may be converted into the form: $A = a \exp(h\Delta E)$ suggesting that a plot of $\ln A$ versus ΔE for the variously doped solid samples should give a straight line. In fact, straight lines were obtained upon plotting $\ln A$ versus ΔE for different investigated solids. The slope and intercept of these lines (not given) permitted a ready determination of the values of the constants "h" and "a". The calculated values of h (mol kJ^{-1}) and a (min^{-1}) are given in Table 3 for pure and treated solid catalysts precalcined at different temperatures. The constants h and a indicate that the treatment process did not modify the dissipation of active sites, i.e. the character of surface heterogeneity. In other words, the treatment of CuO and Co$_3$O$_4$ with Co^{2+} and Cu^{2+} ions did not change the energetic nature of the active sites but increased the number of these sites.

3.3.2. Catalytic decomposition of H$_2$O$_2$ over the investigated solids

The kinetics of the decomposition of H$_2$O$_2$ in the presence of the pure and doped samples calcined in air at 300–700 °C were monitored by measuring the volume of oxygen liberated at different time intervals at 30–50 °C until equilibrium was attained at each temperature. The results obtained showed that the reaction follows first-order kinetics in all cases. In fact, the plots of $\ln(a/(a-x))$ versus time give straight lines, where a is the initial concentration of H$_2$O$_2$ solution (mmol l^{-1}) and x the fraction of H$_2$O$_2$ (mmol l^{-1}) at a given time. The slopes of the first-order plots allow ready determination of the reaction rate constant (k), measured at a given temperature over a given catalyst sample.

Fig. 5 depicts representative first-order plots of the catalytic reaction carried out at 30 °C over pure and variously doped Co$_3$O$_4$ and CuO solids precalcined

at 700 °C. The different values of k for the reaction carried out at 30, 40 and 50 °C over the investigated solid catalysts were calculated. The treatment of CuO with cobalt oxide or the treatment of Co$_3$O$_4$ with copper oxide followed by calcination at 300–700 °C resulted in a progressive increase in the catalytic activity of the treated solids. The maximum increase in the value of $k_{40\,°C}$ attained 528, 228 and 129% for CuO solids treated with 7.5 mol% cobalt oxide calcined at 300, 500 and 700 °C, respectively. While the maximum increase in the value of $k_{40\,°C}$ attained 22.5 and 39.3% for Co$_3$O$_4$ solids treated with 7.5 mol% CuO precalcined at 300 and 700 °C, respectively. The observed remarkable increase in the catalytic activity of the treated solids due to CoO or CuO doping calcined at 300–700 °C in H$_2$O$_2$ decomposition could be attributed to creation of new ion pairs involved in the catalytic reaction. The catalytic reaction proceeds on the catalytic sites constituted from the ion

Table 4
Reaction rate constant per unit area ($\bar{k}$, min^{-1} m^{-2}) for the catalytic decomposition of H$_2$O$_2$ over pure and treated solids precalcined at 300–700 °C

Catalyst	Calcination temperature (°C)	$\bar{k}_{30\,°C}$	$\bar{k}_{40\,°C}$	$\bar{k}_{50\,°C}$
Pure CuO	300	0.073	0.152	0.285
+1.0 mol% CoO	300	0.144	0.30	0.575
+2.5 mol% CoO	300	0.258	0.503	0.981
+5.0 mol% CoO	300	0.335	0.677	1.35
+7.5 mol% CoO	300	0.52	1.05	2.09
Pure CuO	500	0.016	0.037	0.084
+1.0 mol% CoO	500	0.026	0.057	0.107
+2.5 mol% CoO	500	0.038	0.08	0.158
+5.0 mol% CoO	500	0.054	0.111	0.235
+7.5 mol% CoO	500	0.088	0.19	0.36
Pure CuO	700	0.016	0.029	0.063
+1.0 mol% CoO	700	0.024	0.045	0.095
+2.5 mol% CoO	700	0.031	0.064	0.12
+5.0 mol% CoO	700	0.041	0.084	0.167
+7.5 mol% CoO	700	0.053	0.10	0.213
Pure Co$_3$O$_4$	300	0.302	0.453	0.911
+2.5 mol% CuO	300	0.357	0.530	1.084
+5.0 mol% CuO	300	0.413	0.60	1.266
+7.5 mol% CuO	300	0.494	0.694	1.472
Pure Co$_3$O$_4$	700	0.028	0.052	0.111
+2.5 mol% CuO	700	0.034	0.069	0.139
+5.0 mol% CuO	700	0.046	0.091	0.185
+7.5 mol% CuO	700	0.058	0.115	0.229

pairs which in the one ion occurs in a lower and the second in a higher oxidation state (bivalent catalytic sites) [43–45]. The created ion pairs for pure CuO or Co_3O_4 solids are Cu^+–Cu^{2+} or Co^{2+}–Co^{3+}, respectively, while the possible created ion pairs in the treated solids are Cu^+–Co^{3+}, Cu^{2+}–Co^{2+} in addition to ion pairs Cu^+–Cu^{2+} and Co^{2+}–Co^{3+}.

On the other hand, the catalytic activity of pure and variously doped solid catalysts decreased upon increasing their calcination temperature from 300 to 700 °C. The interpretation of these results could be discussed in terms of the possible changes in the concentration of ion pairs acting as active sites for the catalyzed reaction. The variation of reaction rate constant k as a function of cobalt oxide concentration for H_2O_2 decomposition carried out at 30 and 40 °C over pure and variously doped CuO catalysts precalcined at 300–700 °C is graphically represented in Fig. 6. The observed changes in the catalytic activity of pure and treated solids due to calcination at temperatures

ranged from 300 to 700 °C could result from the induced changes in their specific surface areas. In order to account for the observed changes in the S_{BET} due to increasing the calcination temperature of various solids, the reaction rate constant per unit surface area ($\bar{k}$) was calculated for each catalyst sample and given in Table 4.

Determination of the apparent activation energy (ΔE) for the catalysis of H_2O_2 decomposition over different investigated solids shed some light on the possible change in the mechanism of the catalyzed reaction and hence gives useful information about possible changes in the concentration and nature of the catalytically active constituents. The values of k measured at 30–50 °C over pure and variously doped solids enable ΔE to be calculated by direct application of the Arrhenius equation. The calculated values of ΔE are give in Table 5. Inspection of the data listed in Table 5 revealed that the treatment of CuO or Co_3O_4 solids with cobalt ions or copper ions, respectively,

Table 5
Activation energies (ΔE and ΔE^*) and frequency factor for the catalytic decomposition of H_2O_2 over pure and treated solid catalysts calcined at different temperatures

Catalyst	Calcination temperature (°C)	ΔE (kJ mol^{-1})	$\ln A$	ΔE^* (kJ mol^{-1})	Constants h and a
Pure CuO	300	75.4	27.68	75.4	$h = 0.325$, $a = 20.1$
+1.0 mol% CoO	300	56.3	20.99	73.7	
+2.5 mol% CoO	300	53.9	20.52	78.2	
+5.0 mol% CoO	300	56.3	21.77	71.9	
+7.5 mol% CoO	300	55.5	21.85	72.9	
Pure CuO	500	67.1	23.03	67.1	$h = 0.324$, $a = 2.72$
+1.0% CoO	500	58.0	19.8	66.3	
+2.5 mol% CoO	500	58.0	20.06	65.7	
+5.0 mol% CoO	500	58.8	20.62	65.1	
+7.5 mol% CoO	500	57.2	20.38	64.0	
Pure CuO	700	56.8	18.53	56.8	
+1.0 mol% CoO	700	56.3	18.71	55.9	
+2.5 mol% CoO	700	56.3	18.97	55.2	
+5.0 mol% CoO	700	56.8	19.31	54.7	
+7.5 mol% CoO	700	56.3	19.20	54.6	
Pure Co_3O_4	300	57.2	22.8	57.2	$h = 0.342$, $a = 33.1$
+2.5 mol% CoO	300	45.6	18.4	57.0	
+5.0 mol% CoO	300	44.7	18.1	56.8	
+7.5 mol% CoO	300	44.7	18.2	56.4	
Pure Co_3O_4	700	55.9			
+2.5 mol% CoO	700	58.0			
+5.0 mol% CoO	700	57.2			
+7.5 mol% CoO	700	55.0			

followed by precalcination at 300–700 °C brought about a progressive decrease in the ΔE values. These results express the observed progressive increase in the catalytic activity of the investigated solids due to treatment with Co^{2+} or Cu^{2+} ions. The plot of $\ln A$ versus ΔE of the catalytic reaction H_2O_2 decomposition should give a straight line, whose slope and intercept would allow the evaluation of the constant "h" and "a", respectively. Straight lines were obtained upon plotting $\ln A$ versus ΔE (not given) for H_2O_2 decomposition conducted over pure and doped solids. The values of frequency factor ($\ln A$), activation energy ΔE^* and constants "h" and "a" are given in Table 5. Similar conclusion has been obtained as previously mentioned in the catalytic oxidation of CO by O_2 over the pure and treated solid catalysts.

The comparison between the effects of treatment of Co_3O_4 and CuO solids with Cu^{2+} and Co^{2+} ions on their catalytic activities towards CO oxidation by O_2 and H_2O_2 decomposition suggested that the catalytically active sites involved in both catalytic reactions are different from each others. This conclusion is based on the fact that the doping process effected different changes in their catalytic activities in catalyzing both reactions.

4. Conclusions

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

1. The treatment of CuO solid with 7.5 mol% Co^{2+} ion followed by calcination at 300 °C resulted in an effective increase in its particle size (from 80 to 160 Å), while the treatment of Co_3O_4 solids with 7.5 mol% Cu^{2+} ions resulted in a limited increase in its particle size (from 115 to 131 Å).
2. The doping of both CuO and Co_3O_4 solids with cobalt and copper species followed by calcination at 300–700 °C brought about a significant decrease in their specific surface areas.
3. Doping of CuO with cobalt ions followed by calcination at 300 °C brought about a significant decrease in its catalytic activity towards CO oxidation by O_2. While the calcination of treated solids at 500 and 700 °C resulted in a measurable increase in their catalytic activities.
4. Doping of Co_3O_4 solids with copper species followed by precalcination at 300 and 700 °C resulted in a small decrease (about 8%) in their catalytic activity ($\bar{k}_{125\,°C}$ and $\bar{k}_{175\,°C}$, respectively) towards CO oxidation.
5. The treatment of CuO with cobalt ions and Co_3O_4 with copper ions resulted in a measurable increase in their catalytic activities towards H_2O_2 decomposition. The increase was, however, more pronounced in the case of CuO treatment, in which Co_3O_4 solid was very active towards H_2O_2 decomposition.
6. The maximum increase in the catalytic activity of CuO ($\bar{k}_{40\,°C}$) towards H_2O_2 decomposition due to the addition of 7.5 mol% cobalt ions attained 590, 413 and 245% for the solids precalcined at 300, 500 and 700 °C, respectively. While the maximum increase in the catalytic activity ($\bar{k}_{40\,°C}$) of Co_3O_4 due to the addition of 7.5 mol% copper ions attained 53 and 121% for the solids precalcined at 300 and 700 °C, respectively.
7. Treatment of CuO solids with Co^{2+} ions and Co_3O_4 solids with Cu^{2+} ions did not modify the mechanism of the catalytic reaction but increased the number of catalytically active sites (created ion pairs on the outermost surface layers of the treated solids) without changing their energetic nature.

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