Influence Li$_2$O-Doping on Oxide Surface and Catalytic Properties of CuO/Co$_3$O$_4$ Solids

H.M. Arafa

Chemistry Department, Faculty of Science, Tabuk University; P.O.Box 741 Tabuk 71491, Saudi Arabia

ABSTRACT

The effect of Li$_2$O-doping on solid-solid interaction, surface and catalytic properties of CuO - Co$_3$O$_4$ were investigated using XRD, nitrogen adsorption at -196°C and catalytic oxidation of CO by O$_2$ at 150-250°C. The nominal composition of the system was 0.2CuO/Co$_3$O$_4$ and the amount of dopant was varied between 0.75 and 3 mol% Li$_2$O. The results obtained revealed that Li$_2$O-doping inhibited the solid-solid interactions between the mixed oxides precalcined in air at 600°C and decreased the degree of crystallinity and particle size of Co$_3$O$_4$ phase. This treatment led also to a decrease in the specific surface areas of the doped adsorbents precalcined at different temperatures. The catalytic activities towards CO-oxidation by O$_2$ of pure solids decreased progressively by increasing the precalcination temperatures in the range 400-600°C. The doping process brought about a significant increase in the catalytic activities. Lithia doping of the investigated system did not modify the mechanism of the catalytic reaction but changed the concentration of the catalytically active centers without changing their energetic nature.

Key words: Li$_2$O-doping, CO-Oxidation- CuO/Co$_3$O$_4$, XRD

INTRODUCTION

Catalytic oxidation is the process thought by many research studies to curb CO emissions of combustion engines into the atmosphere [1]. Oxidation of carbon monoxide has been carried out on various catalysts. These catalysts are precious metals [2,3] and transition metal oxide catalysts [4–9]. The activity of a catalyst is sometimes remarkably improved by combining more than two elements (synergism) [10–13]. 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$_2$O and Cu as functions of temperature and oxygen partial pressure [14–17], while the oxidation state of cobalt changes between CoO, Co$_3$O$_4$ and Co [18-20]. The effects of lithium content and calcination temperature on different surface properties of CuO/Co$_3$O$_4$ were investigated [21].However, to the author's knowledge, the effect of lithium oxide on the CuO/Co$_3$O$_4$ system have not been yet investigated. The present work aimed to investigate the role of small amounts of Li$^+$ additives in modifying the surface and catalytic properties of CuO/Co$_3$O$_4$ solids. The techniques employed were XRD, nitrogen adsorption at −196$\circ$C, oxidation of CO by O$_2$ at 150–250 $\circ$C.

EXPERIMENTAL

Materials: Co$_3$O$_4$ solid sample were prepared by the thermal decomposition of basic cobalt carbonate at 400 and 600$\circ$C. Samples impregnated with copper were obtained by treating a known mass of finely powdered basic cobalt carbonate with a calculated amount of copper nitrate (0.25 wt.%). The paste was dried at 100 $\circ$C to constant weight. The variously doped solid samples were obtained by treating the dried sample with calculated amounts of lithium nitrate. The paste was dried at 100 $\circ$C to a constant weight then heated in air at 400 and 600 $\circ$C for 4 h. The concentrations of Li$_2$O dopant expressed as mol% were 0.75, 1.5 and 3 mol%. All chemicals employed were of analytical grade as supplied by BDH and Fluka.

Techniques: An X-ray investigation of pure and variously doped solid samples preheated in air at 400& 600 $\circ$C was carried out using a Philips diffractometer (type PW 1390). The patterns were run with Fe-filtered cobalt (λ = 1.7889 Å) for pure

and variously treated CuO/Co_3O_4 solids at 30 kV and 10mA with a scanning speed of 2° in 2θ min−1. 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: $d = K\lambda\ B_{1/2}\ cos\ \theta$ 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 $2\theta\ min^{-1}$. 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 measure-ments, 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. The kinetics of the catalytic reaction was 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 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.

RESULTS AND DISCUSSION

The X-ray diffractograms of pure and variously doped solids precalcined at 400 and 600 °C were measured (not given). The diffractograms of pure and doped Li_2O solid samples precalcined at 400 and 600 °C revealed that the pure solid samples preheated at 400 and 600 °C consisted of Co_3O_4 phase of higher degree of crystallinity, while the doped solids (treated with 3 mol% Li_2O) consisted of Co_3O_4 phase besides CuO as separate phase. The absence of any diffraction line of CuO phase in the pure sample might suggest a complete dissolution of the CuO lattice forming CuO- CoO solid solution and/or the presence of CuO 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 $Cu_xCo_{1-x}O$, where $x \leq 0.25$. The detection of copper oxide as a separate phase in the sample doped with 3 mol% Li_2O might indicate that Li_2O dissolves in the lattice of Co_3O_4 and facilitates the separation of CuO as a crystalline separate phase that could be detected. The increase in the calcination temperature of the solids investigated up to 600 °C resulted in a significant increase in the degree of crystallinity of the produced CuO phase. In fact, the addition of increasing amounts of Li_2O followed by calcination at 400–600 °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 1.50Å from 186 to 210, 166 to 212 and 37 to 43 (a.u.), respectively, upon the addition of 3 mol% Li_2O solids percaline at 400 °C. These findings indicate clearly that CuO doping of Co_3O_4 conducted at 400 and 600 °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 claimed at 400 °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 160Å in the pure sample and those treated with 0.75, 1.5 and 3 mol% Li_2O percaline at 400°C, respectively. So, it can be concluded that CoO - CuO solids doped with Li_2O followed by calcination at 400 and 600 °C brought about a significant increase in the degree of crystallinity and particle size of CuO phase.

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 - Co_3O_4 due to doping with Lithium ions followed by calcinations at 400–600 °C were found to suffer a progressive decrease to an extent proportional to the amount of dopants added. However, the maximum decrease in the S_{BET} of Co_3O_4 - CuO due to doping with Li^+ ions followed by calcination at 400 and 600 °C attained 20 and 37%. The observed decrease in the S_{BET} of CuO -Co_3O_4 due to doping might be discussed in terms of an effective increase in the particle size of CuO & Co_3O_4 phases and possible formation of solid solutions. In fact, X-ray line broadening analysis of treated solids 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.

The catalytic oxidation of CO by O_2 was carried out over pure and variously doped solids preheated at different temperatures (150–250 °C). The results showed that the catalysis of CO oxidation by O_2

follows first-order kinetics over various investigated catalysts. Fig. 1 depicts representative first-order plots of CO oxidation by O_2 conducted at 150 over pure and doped Li_2O solids percaline at 400 °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 preheated at 400 and 600 °C were determined. The variation of k for the reaction conducted at 150–250 °C as a function of dopant concentration is graphically illustrated in Fig. 2 for pure and different doped solids percaline at 400–600 °C. It is seen from Fig. 2 that cobalt oxide doping of CuO solids followed by calcination at 400 °C resulted in a progressive decrease in the catalytic activity of the treated solids while heating the doped solids at 600 °C affected a remarkable progressive increase in the catalytic activity of the treated solids. The observed significant decrease in the catalytic activity of CuO –CoO solids calcined at 400 °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 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 lead to a decrease in its catalytic activity. The significant effective increase in the catalytic activity of CuO solids doped with Li^+ ions followed by calcination at 600 °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. 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 400 and 600°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 [22]. 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.

Determination of apparent activation energy 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 400–600 °C have enabled activation energy to be calculated by direct application of the Arrhenius equation.

However, the computed values are given in Table 2. These results express the observed progressive decrease in catalytic activity of the investigated solids due to doping with CuO followed by calcination at 400 and 600 °C resulted a progressive increase in the activation energy values. These results ran parallel to the observed progressive decrease in the catalytic activity of the investigated solids.

Conclusions

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

1. The treatment of Co_3O_4 solid with 2.5 wt% Cu^{2+} ion followed by calcination at 400 °C resulted in an effective increase in its particle size (from 80 to 160 Å).
2. The doping of both CuO and Co_3O_4 solids with lithium ions followed by calcinations at 400–600 °C brought about a significant decrease in their specific surface areas.
3. Doping of Co_3O_4 with copper ions followed by calcinations at 400 °C brought about a significant decrease in its catalytic activity towards CO oxidation by O_2. However, the calcination of treated solids at 600°C resulted in a measurable increase in their catalytic activities.

Table 1 Specific surface areas for the undoped and doped solids calcined at different temperatures

Solid Sample	S_{BET} (m^2/g)	
	400°C	600°C
Pure CuO/Co_3O_4	33	24
+ 0.75 Li^+	32	22
+ 1.5 Li^+	33	20
+ 3.0 Li^+	31	18

Table 2 Activation energies for the catalytic oxidation of CO by O_2 over pure and treated catalysts calcined at 400 and 600°C

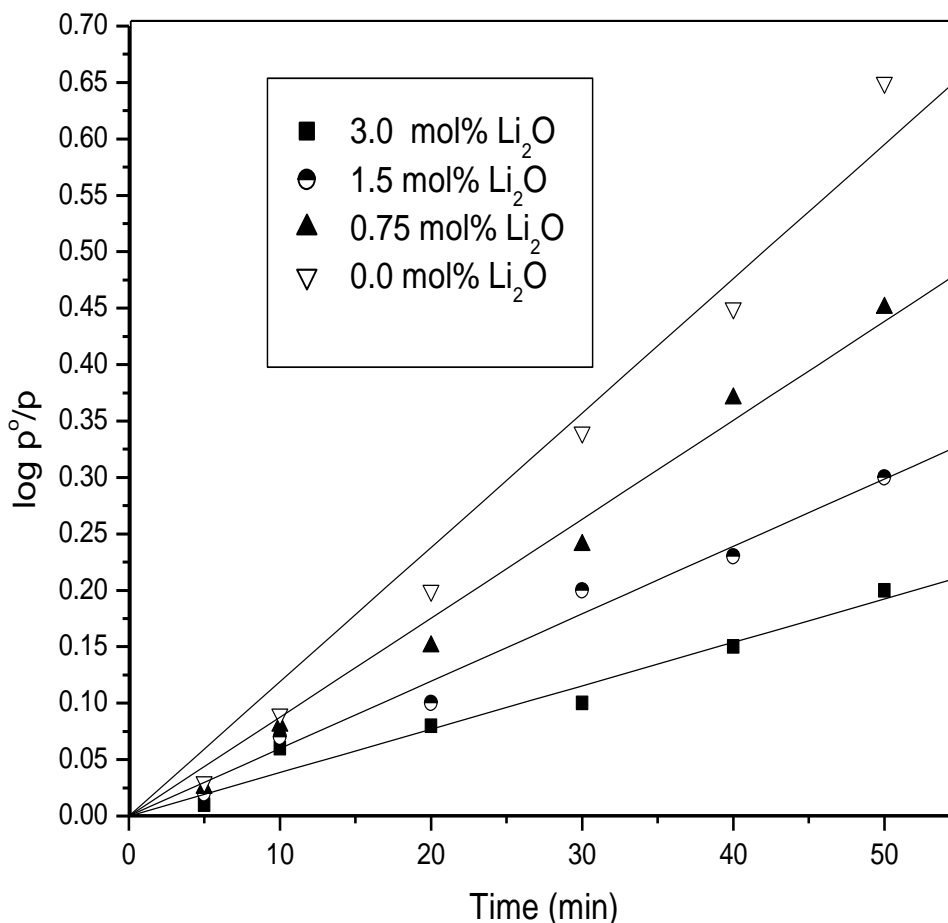| Solid Sample	Activation energy (kJ mol^{-1})	
	400°C	600°C
Pure CuO/Co$_3$O$_4$	34	47
+ 0.75 Li$^+$	28	30
+ 1.5 Li$^+$	25	20
+ 3.0 Li$^+$	20	16

Fig.1 First order plot of CO-Oxidation by O_2 at 150°C for pure and doped CuO-Co$_3$O$_4$ calcined in air at 400°C
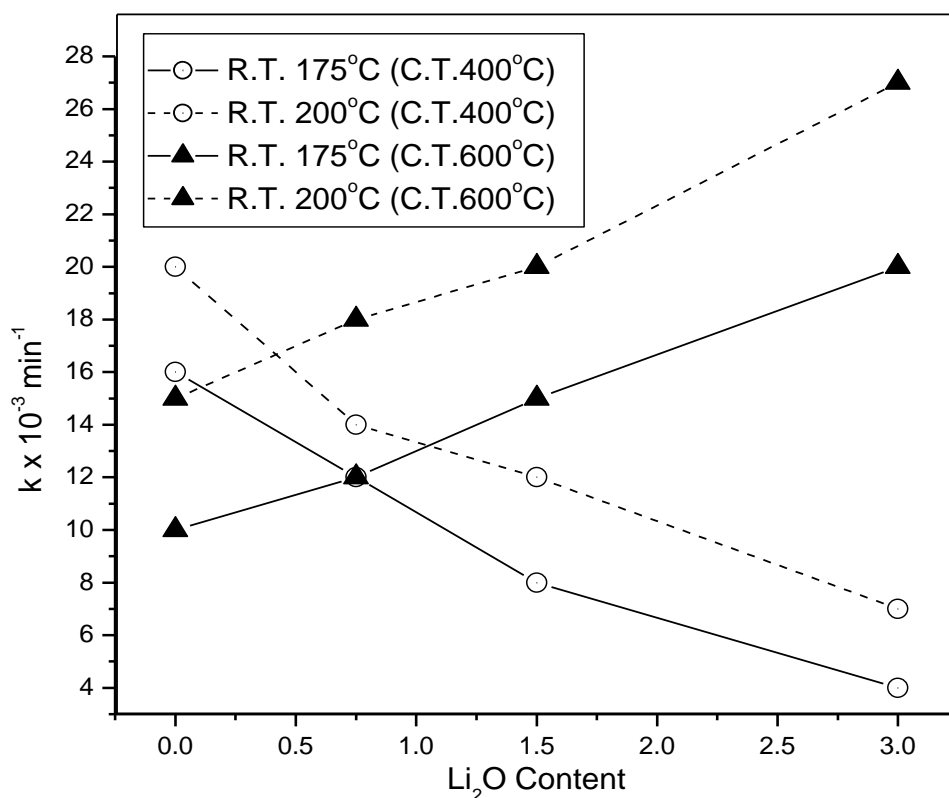
Fig.2 Effect of Li_2O content on the reaction rate constant (k) measured at different reaction temperatures for solids calcined at 400 and 600°C

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